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REMEDIATION INVESTIGATION AND FEASIBILITY STUDY FOR “INPLACE” MINE WASTE INFLUENCED GROVE GULCH, BUTTE, MT

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REMEDIATION INVESTIGATION AND FEASIBILITY STUDY FOR “IN-PLACE” MINE WASTE INFLUENCED GROVE GULCH, BUTTE, MT

by

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Abstract

Historical mining activities in Butte, Montana contributed to the deposition of heavy metal contaminated mine waste/tailings along the tributary streams of the Clark Fork River. These tributary streams, Silver Bow Creek (SBC), Blacktail Creek (BTC), and Grove Gulch make up the headwaters of the Clark Fork River, which flows through western Montana. SBC is currently impaired for arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), zinc (Zn), and sedimentation (MTDEQ, 2016). BTC is the headwaters of SBC, while Grove Gulch discharges into BTC. Grove Gulch is an intermittent stream south of Butte, that is approximately 6 miles in length. The Grove Gulch watershed is the location of the historic Timber Butte Zinc Mill, which throughout its thirty-five-year life produced an estimated one million cubic yards of tailings that were impounded along the path of Grove Gulch. These “in-place” tailings have since been buried, capped (with a geotextile membrane), and developed into the Copper Mountain Recreational Complex (CMRC), but mine tailings are still present in the watershed and creek.

The aim of this study is to characterize Grove Gulch Creek and its watershed, identify heavy metal sources, and conduct a feasibility study. Grove Gulch Creek spatial sample analysis data suggest that the concentrations are significantly elevated immediately downstream of the wooden culvert discharge and decrease as the creek flows towards BTC. Of the ninety-five water samples analyzed, 42% exceeded aquatic life standards and 18% exceeded human health standards for at least one heavy metal. Soil sampling results identified small patches of mine waste around the perimeter of the CMRC. In general, As, Cu, Pb, Zn were elevated in these mine waste patches, however, two of the twenty-seven samples exceeded recreational human health standard for arsenic. Heavy metal concentrations in the streambed and banks varied spatially along Grove Gulch with higher concentrations near the wooden culvert and trailer park areas.

A feasibility study was conducted to evaluate the Best Management Practices (BMPs) based on technical feasibility, cost-benefit analysis, environmental benefits, and human health and safety. Given the complex nature of sources (groundwater, soil, and runoff), the study recommends a combination of three remedial options. A retention basin could be constructed on Grove Gulch before the confluence with BTC to capture runoff and precipitate sediments and associated adsorbed heavy metals. A sulfate reducing bio-reactor could be used to capture and treat the metal-laden groundwater discharge from the wooden culvert. Stabilization of exposed mine tailing and revegetation along the CMRC perimeter would minimize weathering and reduce risk to recreational users in the area. Together these three remedial options could reduce the human health risk along the lower section of Grove Gulch and also reduce the heavy metal loading into BTC.

Keywords: Heavy Metals, Grove Gulch, Butte, Montana, Characterization, Feasibility Study, Mine Tailings

Dedication

I wish to thank my parents Tom, Renee, Mike and brother Cody for all of their love and support throughout my life. Without their words of wisdom and guidance, I would not have challenged myself to get to where I am today.

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Glossary of Terms (optional)

Term	Definition
EPA	Environmental Protection Agency
BSB	Butte-Silver Bow
ARCO	Atlantic Richfield Company
MTDEQ	Montana Department of Environmental Quality
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
GG	Grove Gulch
SBC	Silver Bow Creek
BTC	Blacktail Creek
BMP	Best management practice
NPS	Non-point source
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
QA/QC	Quality assurance/Quality Control
DI	Deionized water
USGS	United States Geographical Survey
RCRA	Resource Recovery and Conservation Act
TSS	Total suspended solids
TDS	Total dissolved solids
MDL	Minimum detection limit
LDL	Lower detection limit
MBMG	Montana Bureau of Mines and Geology
GWIC	Ground Water Information Center
GIS	Geographic Information System
CMRC	Copper Mountain Recreational Complex
TMDL	Total maximum daily load
CFS	Cubic feet per second
SCS	Soil Conservation Service
SQG	Soil Quality Guidelines
COC	Contaminant of Concern

1. Introduction

1.1. Heavy Metals in the Environment

Heavy metals naturally occur in the environment and some like copper, iron, magnesium, manganese, nickel, and zinc are very beneficial if present in the correct concentrations. These micronutrients are often considered trace elements because they often only occur in the parts per billion (ppb) concentrations in the environment and do not pose any adverse health effects. Micronutrients can affect the cellular organelles, cell membranes, and enzymes involved in metabolism, detoxification and repairing cells (Tchounwou, Yedjou, Patlolla, & Sutton, 2012). In elevated levels, heavy metals become toxic to humans, animals, and plants by disrupting natural processes and can cause many different health effects or be carcinogenic. Arsenic for example, often detectable in low concentrations in the environment, can impair cellular respiration by inhibiting mitochondrial enzymes if exposed in the right form and sufficient dosage (Tchounwou et al., 2012).

Anthropogenic activities such as mining, smelting, industrial manufacturing, and agricultural activities can produce environmental contamination that leads to increasing human health exposure. Environmental contamination can originate from mining activities, for example, by smelter atmospheric deposition of metals, soil erosion, leaching of contaminants, sediment re-suspension, and weathering (Tchounwou et al., 2012). Once released into the environment, heavy metals can be mobilized from their original location and often contaminate more complicated systems like stream channels and groundwater. One example of the mobilization of heavy metals is the mining activity and associated mine waste disposal in and around Butte, Montana and how it was transported all the way to the Milltown Dam, 120 miles away in Bonner, Montana. Mining in Butte, particularly copper mining, helped electrify the country during WWII but came at a steep environmental cost (PBS, 2017). The mining in Butte produced mine waste dumps and tailings impoundments that littered the Butte hillside. The combination of this historical pollution led to the listing of Butte and the surrounding area as a Superfund site in 1983 by the Environmental Protection Agency (EPA) under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (USPEA, 2005). The mine waste dumps have been capped and restoration has begun. Currently, a major portion of the work is focused on the stabilization and removal of these "in place wastes" to prevent future contamination.

The effects of pollution on human health is a major concern and the major driving force for the cleanup of the Butte Superfund site. Some of the contaminant of concerns (COC) for the Superfund site such as arsenic, lead, and cadmium are known carcinogens and can cause cancer in elevated levels. Potential health effects from long-term exposure to arsenic are skin damage, circulatory systems issues, and increased risk of cancer. Long-term exposure potential health effects from copper have been associated with liver and kidney damage. Increased exposure from lead can cause delayed physical and mental development in children and kidney problems in adults (USEPA, 2009).

1.2. Grove Gulch

Grove Gulch is a north-northeast flowing creek approximately 6 miles long that drains a watershed roughly 7 square miles into Blacktail Creek (BTC), which is a headwater stream for Silver Bow Creek (SBC) (Figure 1). Historically in Butte, Grove Gulch flowed north along the cemetery located along South Montana Street, but due to flooding issues, it was rerouted to its current path (Figure 1). The rerouting of Grove Gulch resulted in a straight channel ditch along the majority of its lower section with minimal beneficial habitat opportunities. Grove Gulch is mostly fed from annual snowmelt up until the late summer, with groundwater contributing to some portions of baseflow during late summer and the fall. The upper section of Grove Gulch is primarily used for livestock grazing and has multiple private water retention basins along the drainage for livestock. In 1982, the Soil Conservation Service (SCS) flood control project was completed to correct problems associated with flooding due to the placement of the Clark Tailings along the Grove Gulch drainage (Hydrometrics, 1983). The flood control project constructed a retention basin to minimize the impact of heavy storm events which would erode the tailings into lower Grove Gulch and eventually to BTC (Hydrometrics, 1983). This retention basin steadily feeds surface water for the lower sections of Grove Gulch and produces wetland environments along the drainage.

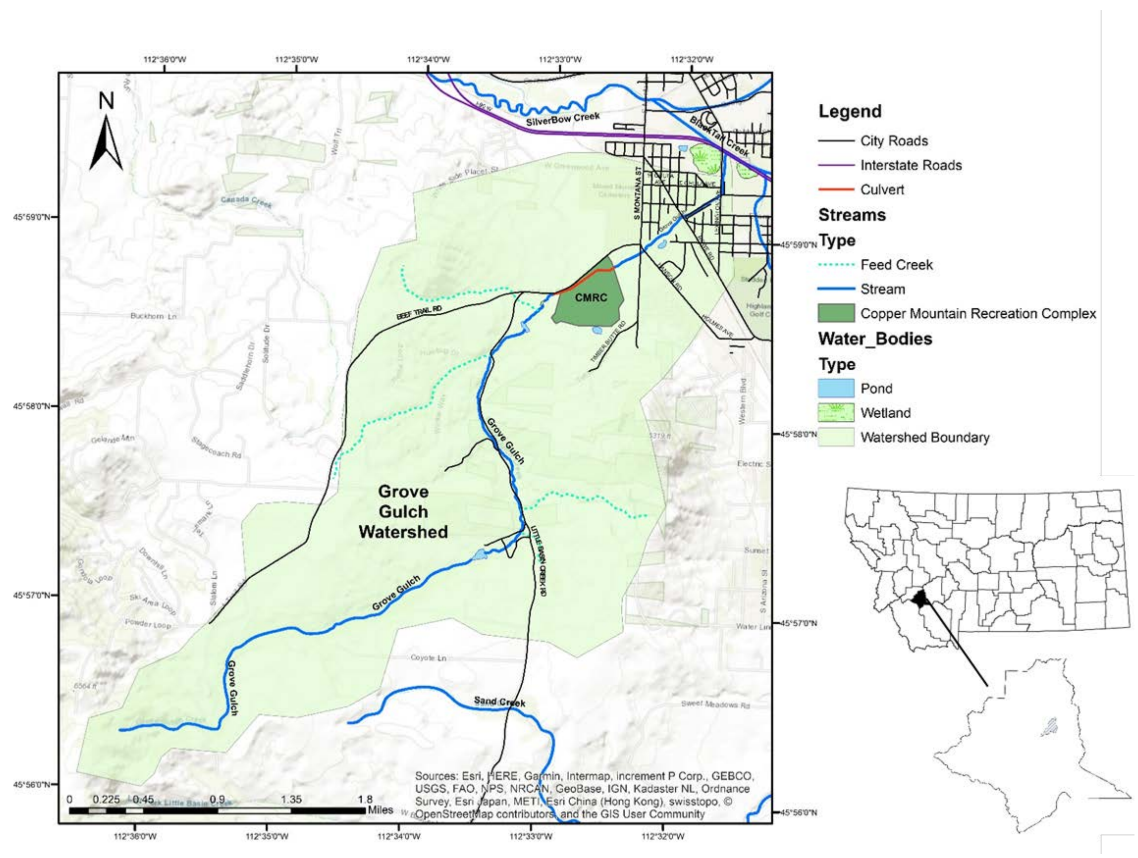

Figure 1: Grove Gulch Watershed location map

1.2.1. Copper Mountain Recreational Complex

The Copper Mountain Recreational Complex (CMRC) is a recreational facility, roughly 200 acres in size and contains baseball fields, a driving range, and other public recreational opportunities. Before being reclaimed and capped, the CMRC was the historical location of the Clark Tailings, the Butte-Silver Bow (BSB) municipal landfill, and the final repository of the Colorado Smelter tailings (Craig, 2016). The long history of industrial activities shaped the surrounding area and lead to the creation of the tailings impoundment located underneath the CMRC today. The reclamation efforts first consisted of slope stabilization producing a 3 to 1 ratio for erosion prevention. Next, a low permeable semi-flexible membrane cover was installed on top of the tailings. After capping of the tailings material, new topsoil was added, and a combination of different native plants was established. A more in-depth description of industrial activities that shaped the CMRC will be discussed individually.

1.2.1.1. Timber Butte Zinc Mill

The Timber Butte Zinc Mill was built in 1914 by William Clark and was located along the northwestern slope of Timber Butte Mountain, which lies roughly two miles south of Butte (Figure 2). The Timber Butte Zinc Mill processed ore from the nearby Elm Orlu Mine (current the Berkeley Pit location) and the then state of the art mill processed roughly 450 tons of ore per day and utilized the latest metallurgical technical advancement for its time. Early assays records from the Elm Orlu mine showed zinc concentrations up to 18% along with other metals such as copper, silver, gold, and lead. Following the death of William Clark in 1925, the Timber Butte Zinc Mill was acquired by the Anaconda Company and ran intermittently until after World War II when it was demolished in 1949 (OXO Foundation, 1973).

With high metal concentrate and throughput, William Clark's zinc mill also produced a considerable amount of tailings waste. During the life of the zinc mill, roughly a million cubic yards of tailings were impounded along the Grove Gulch watershed (Hydrometrics, 1983).

Figure 2: Timber Butte Zinc Mill (USGW Archives, n.d.)

1.2.1.2. Colorado Smelter Tailings

By the turn of the 20th century, there were over a dozen smelters and concentrators along SBC, of those the largest was William Clark's Colorado Smelter and Butte Reduction Works. The Colorado and Montana Smelter Company operated from 1879 to 1905 and produced an estimated 250,000 cubic yards of heavy metal-laden tailings along SBC (Hydrometrics, 1983). During the restoration of SBC, roughly 1.2 million cubic yards of Colorado tailings were removed offsite, and approximately 800,000 cubic yards were mixed with the Clark Tailings along Grove Gulch (US EPA, 2006).

1.2.1.3. Butte-Silver Bow Municipal Landfill

Up until its closure in 1999, the Butte Municipal Landfill resided just west and upstream of the historic Clark Tailings. Both domestic and industrial waste were accepted at the landfill during its operation. Before closure, the Colorado Tailings were moved into a repository on site. Prior to moving the Colorado Tailings a Resource and Conservation Recovery Act (RCRA) corrective action was completed (US EPA, 2006).

1.2.2. Land Use

The Grove Gulch watershed land uses are mostly privately owned with undeveloped property, agricultural grazing, grasslands, and residential neighborhoods. Grove Gulch then flows onto Butte-Silver Bow (BSB) County public land, where it flows northeast through the historical Timber Butte Zinc Milling site and reclaimed waste repository also known as the CMRC (Craig, 2016). After discharging out of a 42-inch concrete culvert below the CMRC, Grove Gulch flows into the city limits of Butte and passes through a combination of BSB property and privately owned residential property where it eventually discharges into BTC.

1.2.3. Hydrology

Grove Gulch is considered an intermittent tributary to BTC. An intermittent stream is defined as a stream located below the shallow groundwater table during part of the year and flows in response to groundwater recharge and precipitation (MTDEQ, 2016a). The primary contribution to flow for Grove Gulch is from annual snowmelt and precipitation during the spring. In 2017 the average snowfall for the Butte area was 62 inches a year and the annual precipitation is roughly 12 inches a year (US Climate Data, 2018). Other sources of flow contribution come from shallow groundwater. There are three types of flow regimes that affect flow conditions on Grove Gulch: base flow, normal high flow, and wet weather flow conditions, which are described in greater detail below.

Upper Grove Gulch is primarily fed from groundwater infiltration during the spring via the Highland Mountain Range. Upstream of the CMRC, there is a constructed retention basin that captures sediment and runoff from the upper reach of Grove Gulch. Shortly after the retention basin Grove Gulch flows into a 42-in concrete pipe and is routed through the waste repository. Grove Gulch then flows through a series of straight channel ditches. It is possible that the lower 900 ft section of Grove Gulch that runs along Lexington Avenue may be fed from groundwater infiltration from nearby wetlands across the street.

1.2.3.1. Flow Regimes

1.2.3.1.1. Baseflow Conditions

Baseflow conditions are defined as periods when groundwater inflow encompasses the largest percentage of flow contribution to surface water (USEPA & MTDEQ, 2017). Typical baseflow conditions range from late July to mid-March, or when spring snowmelt begins. Grove Gulch can freeze at the surface if outside temperatures drop below freezing for extended periods of time but water still flows below the ice which was observed in December of 2017.

1.2.3.1.2. Normal High Flow Conditions

Normal high flow conditions are defined as elevated flow above normal baseflow conditions, usually from snowmelt where no precipitation events are occurring (USEPA & MTDEQ, 2017). Normal high flow conditions on Grove Gulch range from mid-March through early July depending on snowpack and daily temperatures. Precipitation events do occur during normal high flow conditions but these are classified as separate flow events.

1.2.3.1.3. Wet Weather Flow Conditions

Wet weather flow conditions are considered storm events that provide fast deposition of rain or snowmelt over a short period of time. Wet weather flow can elevate flow above baseflow conditions or normal high flow conditions (USEPA & MTDEQ, 2017). Typical rainy conditions in the Butte area happen from April to late June as well as September. Early heavy snow followed by high temperatures can also contribute to wet weather flow conditions.

1.2.4. Stream Characterization

Grove Gulch has a larger stream slope along its headwater reaches, and transitions to a smaller slope along the lower section as it runs through residential areas in Butte. The lower sections of Grove Gulch are mostly straight channels. Due to the lack of sinuosity and low flow velocity, there is a large deposition of sediment material along the bed of the stream causing a buildup of organic and inorganic material. This buildup can reduce the beneficial use of the stream for aquatic life and recreational uses (MTDEQ, 2016a).

1.3. Sources of Heavy Metals

The mining process, which encompasses all the processes for removing and concentrating ore, can generate byproducts like mine waste dumps, tailings impoundments, and slag (from smelting). These byproducts are often impounded near the source of generation because of the low-cost benefits, which was the case for the Clark Tailings and Colorado Tailings. Heavy metals contained in tailings and waste dumps are mainly immobilized but can be introduced into the environment by contact with surface water (by erosion) or groundwater. Heavy metals in ore deposits are relatively immobile, whereas heavy metals in mine waste under the right environmental conditions can transition to dissolved metals and impact groundwater or become mobilized via runoff from precipitation and weathering. Some of these environmental conditions are low oxygen environments where redox-dependent desorption takes place, exhausted adsorption capacity, or pH changes in the water chemistry (Egemose, Sønderup, Grudinina, Hansen, & Flindt, 2015).

1.3.1. Clark & Colorado Tailings Repository

The Clark Tailings, generated as a byproduct of William Clark's Timber Butte Zinc Mill, occupied an area roughly 62 acres. Over a period of 35 years roughly one million cubic yards of heavy metal-laden tailings were produced and are currently impounded along the Grove Gulch. Before production of the tailings, a combination vitrified tile and wood stave pipe was installed to transport the Grove Gulch flow beneath the tailings. This pipeline, however, was undersized and couldn't handle runoff or snowmelt events and deteriorated over time. In 1982 a 42- inch diameter reinforced concrete pipe (Figure 3) was installed to replace the wood and tile pipe (Figure 4) (Hydrometrics, 1983). The concrete culvert is the main culvert used for connecting Grove Gulch above and below the CMRC. The old wood and tile pipe that was originally routed through the tailings is still currently discharging into Grove Gulch next to the concrete culvert (figure 4). Figure 5 shows the present underground location for both the concrete pipe (shown in red) and the old wood pipe (shown in blue) underneath the CMRC.

Figure 3: Current 42-inch concrete culvert connecting upper and lower Grove Gulch

Figure 4: Original combination vitrified tile and wood stave pipe culvert

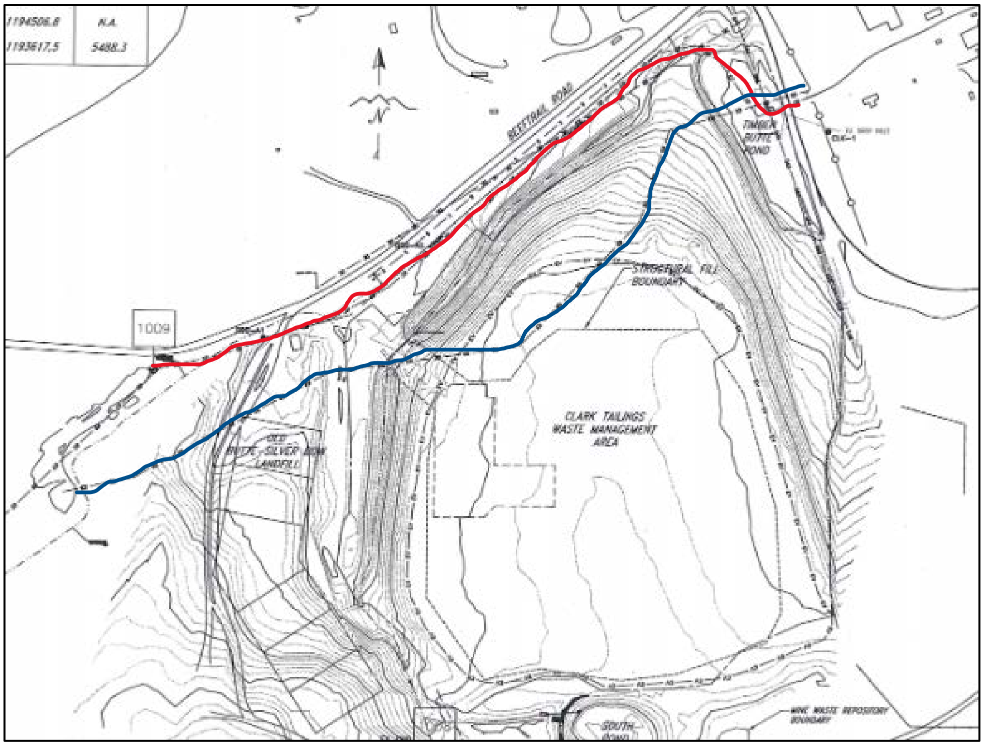

Figure 5: Clark Tailings management area with the concrete culvert (red) and wooden culvert (blue) locations (Pioneer Technical, 2001)

1.3.2. Eroded Mine tailings along Grove Gulch Corridor

Prior to remediation of the Clark Tailings and the Soil Conservation Service flood control project, runoff and heavy snowmelt from upstream Grove Gulch would erode tailings deposits and discharge to lower Grove Gulch and downstream to BTC (Hydrometrics, 1983). These sporadic deposits along the Grove Gulch stream bed and banks can become mobilized by heavy flows, stormwater runoff, and groundwater infiltrating through the deposited material into the surface water of Grove Gulch.

1.4. Grove Gulch Heavy Metal Feasibility Study

1.4.1. Remediation Criteria

To determine the most effective remedial options for Grove Gulch, a set of remediation criteria will be analyzed. The criteria will be used to evaluate the effectiveness of a single or a combination of options to reduce heavy metal contamination in the Grove Gulch watershed. All major remediation activities in the Butte Priority Soils Operable Unit (BPSOU) that apply for funding through the Butte Natural Resource Damage Restoration Council (BNRC) must follow a set of strict guidelines outlined in the "Upper Clark Fork River Basin (UCFRB) Restoration Grants 2009 Application Review Guidelines" developed by the BNRC (BNRC, 2009). These procedures outline the in-depth criteria that must be considered for remedial investigation projects. For the sake of this thesis, only the major criteria for remedial investigations were considered.

1.4.1.1. Technical Feasibility

The technical feasibility of a proposed remedial option assesses the technology and management skills necessary to implement the project. The chance of a successful completion of the project in an acceptable period of time is also considered in the technical feasibility section. A reasonably feasible project employs well-known and accepted technology in design, engineering, and implementation. For innovative technologies, enough research must be available to show the likelihood of achieving the stated objectives. If a remedial option lacks the proper management, implementation steps, or research knowledge in order to a complete the project, the remedial option will have an increased uncertainty (BNRC, 2009).

1.4.1.2. Cost-Benefit Analysis

For a remediation investigation, the expected costs compared to the expected benefits should be weighed in order to determine which option benefits the restoration efforts the greatest. The cost-effectiveness must evaluate whether a project accomplishes goals the least costly way possible. Along with analyzing cost, a project should be compared to alternative methods, one of which should include doing nothing (BNRC, 2009).

1.4.1.3. Environmental Benefits

In order to evaluate the different remedial options, the environmental benefits will be addressed and taken into consideration. The long-term and short-term impacts should be evaluated in order to justify the overall impact on the human environment (BNRC, 2009). With any activity, there is the possibility of creating more problems. The environmental benefits should be weighed against any new adverse impacts when compared to doing nothing. The biological environmental impact should also be investigated.

1.4.1.4. The Benefit to Human Health and Safety

The last remedial criteria that will be used for evaluating the remediation options is the benefit to human health and safety. The proposed remedial options should list the potential benefits to human health and safety by detailing how the anticipated project will reduce heavy metal exposures (BNRC, 2009).

1.5. Performance Standards

Performance standards for surface water quality are defined by Section 12 of the Butte Record of Decision (ROD). Table I shows the applicable numeric water quality standards for the BPSOU addressing surface water quality. For baseflow conditions, chronic aquatic life standards are the required standards promulgated under Circular DEQ-7 numeric water quality standards (MTDEQ, 2012). For normal high flow or wet weather flow conditions, acute aquatic life standards are required under MTDEQ Circular DEQ-7 numeric water quality standards (MTDEQ, 2012). Arsenic, cadmium, copper, lead, and zinc have human health standards set by the maximum contaminant level (MCL) which was adopted by MTDEQ from the EPA (USEPA, 2009).

Table I: Numeric Surface Water Quality Standards (MTDEQ, 2012)

Contaminant	Human Health Standard (µg/L)	Chronic Aquatic Standard (µg/L)	Acute Aquatic Standard (µg/L)	Notes
Arsenic	10	150	340	
Cadmium	5	0.097	0.52	Hardness- Dependent
Copper	1,300	2.85	3.79	Hardness- Dependent
Iron	--	1,000	--	
Lead	15	0.545	13.98	Hardness-Dependent
Zinc	2,000	37	37	Hardness-Dependent

The Montana Circular DEQ-7 numeric water quality standards for aquatic life require acute and chronic standards for cadmium, copper, lead, and zinc to be calculated using the specific sample’s total hardness (mg/L CaCO3). Table II lists the hardness relationships and equations to calculate acute and chronic standards from individual total hardness concentrations.

Table II: Aquatic Life Standards as a Function of Hardness (MTDEQ, 2012)

Metal	Acute		Chronic	
	ma	**ba**	**mc**	**bc**
Cadmium	1.017	-3.924	0.741	-4.719
Copper	0.942	-1.700	0.855	-1.702
Lead	1.273	-1.460	1.273	-4.705
Zinc	0.847	0.884	0.847	0.884
Equations:	**exp.{ma[ln(hardness)]+ba})**		**exp.{mc[ln(hardness)]+bc})**	

1.6. Remediation Options

Different remedial options will be developed and proposed in order to reduce heavy metal exposure along the Grove Gulch watershed. Once different pathways of exposure are understood, a single or combination of remedial options will be proposed and analyzed by the remediation criteria to determine the most feasible option for reducing heavy metals in Grove Gulch.

1.6.1.1. Retention Basins

A retention basin is a manmade or natural structure used to contain large inflows of water and slow the water velocity. Lowering the inflow velocity allows particles and sediments to settle out and deposit along the bed of the basin. A retention basin's effectiveness and efficiency are largely dependent on proper design, monitoring, and maintenance of the best management practice (BMP) (Muthukrishnan, 2006). Sedimentation, the remove suspended sediments, allows heavy metals adsorbed onto the suspended sediments to settle out and deposit in the basin. Both retention basins and vegetated wetlands have been shown to effectively reduce total suspended sediments (TSS) while also reducing concentrations of heavy metals (Muthukrishnan, 2006). Currently, in BPSOU, there are ten detention and retention ponds in use for both peak flow reduction and water quality improvement (Morrison-Maierle & Water & Environmental Technologies, n.d.). In a study completed by the EPA, different types of stormwater BMPs were studied and they predicted roughly 50-80% of metals could be removed by a retention basin along with approximately 70% of suspended solids (USEPA, n.d.).

1.6.1.2. Sulfate-Reducing Bio-Reactor

Sulfate-Reducing bio-reactors (SRBR) utilize organic matter and sulfate-rich water to precipitate and immobilize dissolved heavy metals. Sulfate-reducing bacteria utilize the organic material, such as wood chips, as an electron donor and convert sulfate to sulfide, and then sulfide is used to precipitate out heavy metals. SRBR can achieve removal efficiencies upwards of >99% for dissolved heavy metals in ideal conditions, although some constraints that affect removal efficiency are cold climates, acidic conditions, and oxygen (Moreira, 2018).

1.6.1.3. Soil Remediation

Soil remediation is the process of excavating or removing soils contaminated with heavy metals and transporting to a stabilized in-place tailings repository. Depending on the location, some soil remediation can be done in place. Typically, in-place remediation requires stabilization of tailings material to minimize erosion. After stabilization, a soil cap between 24 inches and 48 inches is added with extra soil in areas requiring tree planting (BNRC & NRDP, 2012). The main goal of soil remediation is to prevent the ingestion of contaminated soils, waste rock or tailings material that would result in an increased risk to human health. Likewise, it's important to prevent the release of contaminated media into aquatic environments increasing the heavy metal loading on surface water (US EPA, 2006).

1.6.1.4. Removal of Old Tile and Wood Stave Pipe

Historically, Grove Gulch surface water quality (prior to being transported beneath the Clark Tailings) has shown low concentrations of heavy metals. Whereas, water sampling below the CMRC has shown elevated levels of heavy metals. One source of heavy metals is the effluent from the old combination tile and wood stave pipe (wooden culvert). This wooden culvert is no longer connected to upstream Grove Gulch and the current discharge is from groundwater. The groundwater in and around the buried Clark Tailings could be flowing towards the wooden culvert and then discharging into Grove Gulch. Remedial options would need to focus on stopping discharge from the wood pipe and prevent groundwater from infiltrating out of the tailings impoundment.

1.6.1.5. Minimizing Groundwater impact on Grove Gulch

Historical sampling of groundwater from the Clark Tailings shows that there is the extensive heavy metal contamination present in elevated levels in the area. The SCS flood control project installed seven groundwater wells along the Grove Gulch and in the Clark Tailings in-order to understand the groundwater heavy metal concentrations. Table III shows the mean heavy metal concentrations for the sampling study with GW-1 starting upstream of the Clark Tailings and GW-6 ending downstream of the Clark Tailings. One remedial option would be to minimize groundwater infiltration along Grove Gulch by lining the channel to reduce heavy metal loading from groundwater.

Table III: Mean Groundwater Concentrations from 1979-1982 (Hydrometrics, 1983)

Sample #	Site Location	Arsenic mg/L	Cadmium mg/L	Copper mg/L	Iron mg/L	Manganese mg/L	Lead mg/L	Zinc mg/L
GW-1	Upstream Basin Cr Rd	0.01	0.01	0.09	0.07	0.28	0.01	0.1
GW-2	0.4 Miles below GW1	0.02	0.01	0.07	1.425	4.59	0.055	0.215
GW-3a	NE Corner county junk car lot	0.06	0.02	0.05	175	1160	0.01	600
GW-3b	SW corner Clark Tailings	0.05	0.02	0.145	17.505	108.5	0.135	25.8
GW-4	Clark tailings 100ft above RR	0.065	0.025	0.315	92.2	261	0.16	133
GW-5	E Side RR below Clark Tailings	0.015	0.01	0.14	25.85	328.5	0.065	110.5
GW-6	S side GG W side Montana St.	0.025	0.015	0.535	17.89	5.685	0.0455	3.195

1.7. Objectives

The objectives of this thesis research on Grove Gulch were:

- Characterize (creek water, sediment, and watershed soil samples)
- Calculate daily loading rates.
- Quantify the difference between total recoverable metals and total dissolved metal concentrations
- Determine heavy metal sources
- Conduct a feasibility study to evaluate remedial options to reduce heavy metal contamination of Grove Gulch, based on technical feasibility, cost-benefit analysis, environmental benefits, and human health and safety.

2. Methods

In order to evaluate the different remedial options, extensive Grove Gulch sampling was completed for surface water, soil and sediment samples. In addition, a comprehensive literature review was conducted to identify the existing data.

Existing data was obtained from the following sources:

- Garrett Craig - *"Characterizing Sources of Nutrient Loading and Heavy Metals and Developing Best Management Practices for Grove Gulch in Butte, MT"*
- USPEA (contact person – Nikia Greene) and downloaded from https://etl.treccorp.com/Trec
- Copper Mountain Recreation Complex as-built drawings from Pioneer Technical Services
- Hydrometrics 1983 Report -*"Summit and Deer Lodge Valleys Long-Term Environmental Rehabilitation Study Butte-Anaconda, Montana Volume 4"*
- Montana Bureau of Mines and Geology – Ground Water Information Center

Data was only used once it was validated to meet specific quality control standards. These standards consisted of following quality control and quality assurance practices for data collection and analysis process. The data from these sources were compiled and analyzed to understand Grove Gulch characteristics. Data compiled included heavy metal characterization of surface water, soil and sediment samples. Water quality data included samples collected during base flow and stormwater runoff conditions.

2.1. Sampling Plan

A sampling plan was developed for the Grove Gulch based on the geographic location, historical impacts and prior research on this drainage. The sampling plan was designed to provide guidance in the field to acquire accurate and high-quality data. The sampling plan was developed from information based in the US EPA Water Sampling Operating Procedure to set strict guidelines when field sampling (USEPA, 2017).

2.1.1. Sampling Strategy

The sampling strategy was developed to determine representative sampling locations. The criteria used for determining sampling locations were based on prior gathered water quality data, geographical data, and specific possible sources of heavy metals. Sampling locations focused on the lower reach of Grove Gulch since prior research has shown increased heavy metal contamination below the Copper Mountain Recreational Complex (CMRC) (Craig, 2016). An upstream location from the CMRC was added to compare elevated heavy metal sources with water that hasn't been exposed to tailings material. The remaining locations were spread out along Grove Gulch to locate possible point source or non-point sources of heavy metal contamination.

2.1.1.1. Soil and Sediment Sample Collection Procedure

Soil samples were selected at random along Grove Gulch. Once a sampling site was selected, all vegetation and large rocks were removed from the surface. For soil samples, a 4 by 4-inch square was excavated and a sample was taken between the depths of 1-6 inches.

Sediment samples were selected at random locations along the Grove Gulch stream bed. Using a clean acid washed stainless steel trowel, the top one-inch layer of organic debris and sediment were removed. Using slicing motions, slices of sediment were sampled and slowly brought up to the surface to reduce the risk of losing material. Samples were collected in a Ziploc bag and excess water was decanted off the sediment sample. All samples were labeled with the sample name, time, date and the name of the sampler.

2.1.1.2. Surface Water Sampling Procedures and Preservation

Specific locations for surface water samples were pre-determined prior to sampling so data could be compared over the course of a year. Prior to sampling, all sample bottles were prewashed with Dawn dish soap and 10% Hydrochloric acid and air dried. Samples were collected in 1-liter sample bottles and then immediately analyzed for pH, temperature (in °C) and specific conductivity. Within 30 minutes of sampling, the 1-liter sample was divided up into two separate 500 mL bottles. The first bottle was filled with 500 mL of unfiltered sample and then preserved with 1.5 mL of concentrated nitric acid. The second bottle was filled with sampled water filtered with a 47mm 0.45-micron nylon MDI Membrane Technologies filter and then preserved with 1.5 mL of concentrated nitric acid. The purpose of acid preservation is to prevent adsorption of metals to sampling container, the precipitation of metals, and to halt any biological activity that might change the valence of an element (USEPA, 1983).

2.1.2. Stream Flow Measurements

Flow measurements in the field followed the USGS midsection methodology. A Marsh McBirney Flo-Mate 2000 flow meter was used to determine the velocity and cross-section depth, and a measuring tape was used to determine the channel width. Prior to stream gaging, the Marsh McBirney would be calibrated in a bucket of water and adjusted before fieldwork was completed. Due to the low flow conditions of Grove Gulch, a cross-section length of 0.5 ft was used to calculate flow rates. At each cross-section, an initial depth measurement would be recorded, and the flow rod would then be adjusted to situate the velocity meter of the Marsh-McBirney at 60% the total depth (Corbett, 1943). Using the cross-section methodology, volumetric flow rates were then determined from area and velocity.

2.1.3. Water Sampling Locations

Sampling locations were spread out along the Grove Gulch watershed drainage mainly focusing along the lower section below the Copper Mountain Recreational Complex. As determined by Montana Tech Masters student Garrett Craig, heavy metal contamination was more localized to the lower section of Grove Gulch centralized around the CMRC downstream to the confluence of Blacktail Creek. A location map with the sampling locations is shown in Figure 6.

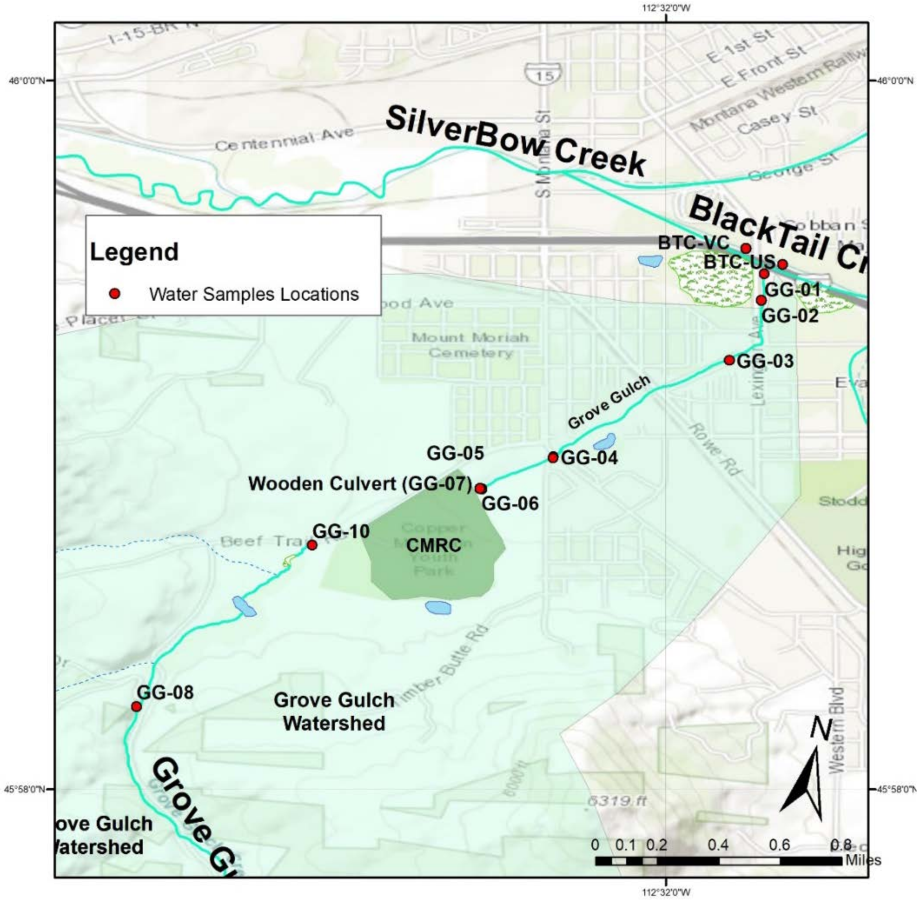

Figure 6: Surface water sampling locations along Grove Gulch

2.1.4. Soil Sampling Locations

Soil sampling was conducted along the Grove Gulch creek and the surrounding watershed. The soil sample locations were randomly selected along varying distances from the stream bank. Soil samples were sampled at a cumulative depth between 1-6 inches. Figure 7 shows the soil sampling locations that have been analyzed using a handheld x-ray fluorescence

(XRF) analyzer. If samples showed elevated levels of heavy metals, the samples were further analyzed at the Environmental Engineering Lab by using an ICP-OES or by the MBMG Analytical Lab. Samples were also cross-analyzed by MarCOM Labs. In total, 53 soil samples were collected and analyzed.

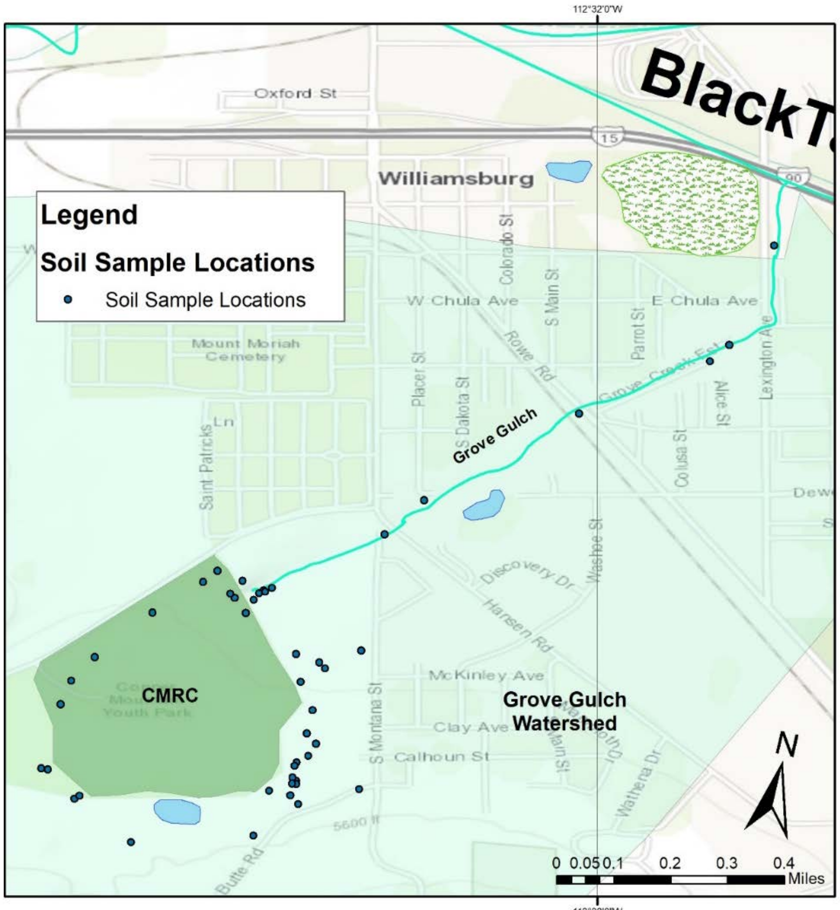

Figure 7: Soil sampling locations along Grove Gulch

2.1.5. Sediment Sampling Locations

Sediment sampling was conducted along the Grove Gulch study reach. Sediment samples were randomly selected along different widths of the creek bed. The depth that samples were taken at ranged between 1-2 inches. Figure 8 shows the sediment sampling locations along

Grove Gulch that have been analyzed with XRF. If samples showed elevated levels of heavy metals, the samples were further analyzed at the Environmental Engineering Lab by using an ICP-OES or by the MBMG Analytical Lab. Samples were also cross-analyzed by MarCOM Labs. In total 58 sediment samples were collected and analyzed.

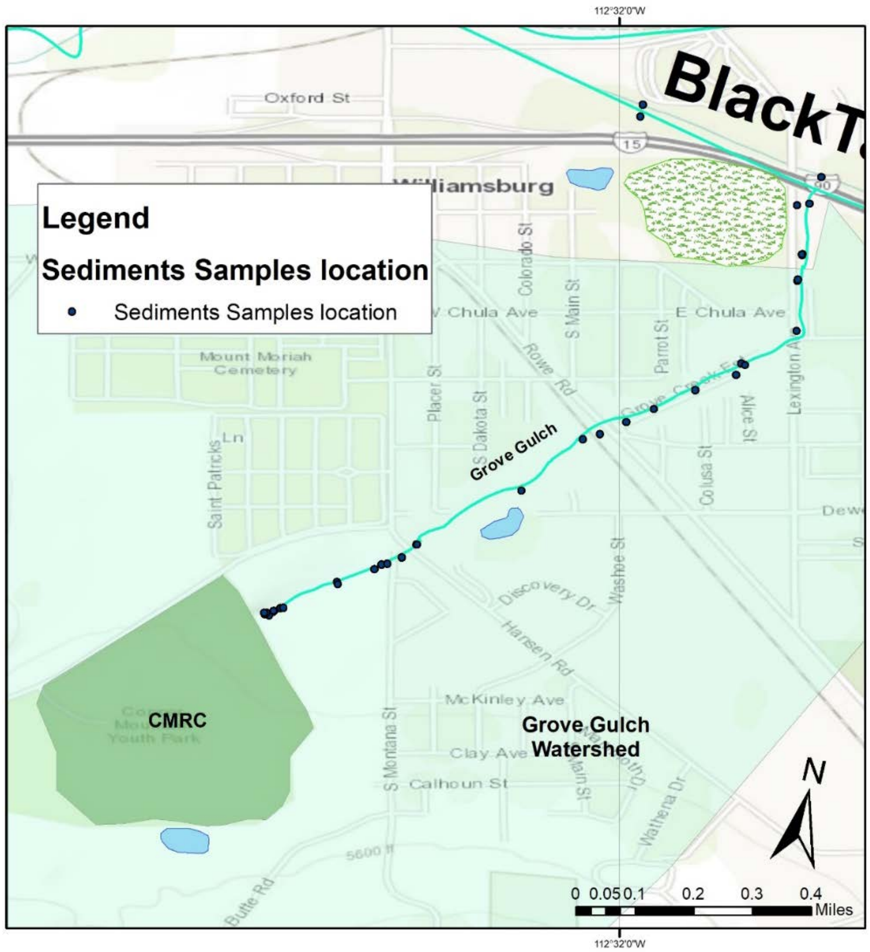

Figure 8: Sediment sampling locations along Grove Gulch

2.1.6. YSI EXO2 Multiparameter Sonde

Two YSI EXO$_2$ multiparameter sondes were used in the field to collect continuous water quality parameter data at two locations on Grove Gulch. YSI sondes can collect high-quality data and are very durable in order to be left out in the field for extended periods of time. The sondes were placed in the field from the fall of 2017 to the fall of 2018, with the exception of a three-month period where they were removed because of freezing conditions. The first location, shown in Figure 9, was located south-west and upstream of the CMRC. This location was selected to show water quality characteristics for Grove Gulch above the CMRC. The second Sonde was located at a man-made weir about 650 ft upstream from the confluence of Grove Gulch and BTC. The second location, shown in Figure 10, gathered data for potentially elevated water quality levels of heavy metals in Grove Gulch. These locations were based on historical sampling done prior to this study.

Figure 9: Upstream sonde location

Figure 10: Downstream sonde location

2.2. Field Quality Control Measures

Field quality control measures were implemented to ensure high-quality data and to prevent sources of error in data collection. All sampling equipment was first washed with Dawn dish soap and water and then with a 10% Hydrochloric acid followed by rinsing with deionized water (DI). Brand new Ziploc bags were used for all soil and sediment samples and new bags were used after each step during sample preparation. Sampling bottles were also washed with a Dawn soap/water mixture and then 10% Hydrochloric acid followed by DI water. All samples were stored in ice during field work to maintain a temperature at or below 4°C.

2.2.1. Field Reagent Blank

Field blanks are bottles filled with DI water in the field. Field blanks are prepared and kept with sampling equipment and bottles for all stages of the sampling process. Field blanks are also digested along with samples and analyzed with the samples. The purpose of this quality control measure is to determine the variability from handling techniques or sample collection (USEPA, 2013).

2.2.2. Field Duplicate

Field duplicates were utilized to show variance in samples taken at the same time (USEPA, 2013). This quality control was used to show that concentrations in samples were consistent and not one-time releases of contaminants.

2.3. Laboratory Analysis

Laboratory analysis utilized multiple different pieces of equipment with specific steps in place to maintain quality control in the lab setting and when analyzing samples. Table IV shows a list of equipment used and the methods followed while running the equipment.

Table IV: Sampling and Analytical Methods

Type of Analysis/Sampling	Equipment	Method
Dissolved Heavy Metals	Thermo Scientific iCAP 6000 Series ICP-OES	EPA 200.7
Sample Preparation for Total Recoverable Elements	Temperature Adjustable Hot Plate	EPA 200.2
Sample Preparation for Sediments, sludges, and soils	MARS 5 Microwave Accelerated Reaction System	EPA 3050B
Temperature, pH, DO, Specific Conductivity, Turbidity	YSI EXO_2 Multiparameter Sonde	N.A.
Flow Rate	Marsh McBirney Flo-Mate 2000	USGS Midsection Method
Water Level	Solinst Levelogger Edge Model 3001	N.A.
GPS Surveying	Trimble R2 GNSS	N.A.
Sulfate	HACH DR6000	TNT 865 (150-900 mg/L SO_4)

2.3.1. Sample Digestion and Preparation

2.3.1.1. Total Recoverable Element Digestion

For total recoverable element digestions, a temperature variable hotplate was used following EPA Method 200. A Seal block digester was used initially but due to the sporadic heating, it was not effectively providing enough heat to digest the sample. TRM samples were digested in a circle pattern around a beaker of DI water to which helped dissipate heat throughout the surrounding six digestion beakers. For TRM, 50 mL of sample was transferred to a 250 mL beaker. Two mL of (1+1) trace metal grade Nitric acid was added to the sampled followed by 1 mL of (1+1) trace metal grade Hydrochloric acid. The sample was then placed on the hotplate and gradually heated to 85°C and evaporated until about 15-20 mL of sample was remaining. After the sample volume was reduced the beakers were covered with a ribbed watch glass and refluxed for 30 minutes (USEPA, 1994). Samples were allowed to cool completely prior to filtration. Samples were then filtered with a .45-µm filter to remove any particles larger than .45-microns which could plug the nebulizer on the ICP-OES. Samples were transferred to a 30 mL syringe with a .45-micron filter attached to the end. Samples were forced through the filter and then both the beaker and syringe were washed with DI water to make sure any remaining sample was transferred to the 50 mL sample vial. DI water was then used to top off the 50 mL vials, and the vials were inverted 20 times to effectively mix the sample. Samples were properly labeled and stored in a 50 mL vial test tube rack in a refrigerator until analysis.

2.3.1.2. Total Dissolved Element Analysis Preparation

From the 1 L sample taken in the field, 500 mL of the thoroughly mixed sample was transferred to a 47-mm diameter, .45-micron filter and a negative pressure pump was used to pull the sample through the nylon filter. DI water was used to rinse out both the graduated filter and the vessel that stored the sample while being filtered. Care was taken to rise down the filter to make sure all dissolved metals made it through the filter process. Care was taken to make sure excess DI water wasn't added and to ensure metal concentrations were diluted. After filtration, the sample was acidified to a pH of <2 with trace grade nitric acid and stored in a refrigerator until analysis.

2.3.1.3. Acid Digestion of Soils and Sediments

EPA Method 3050B for Acid Digestion of Sediments, Sludges, and Soils was followed to digest soil and sediment samples. Soil and sediment samples taken in the field and were returned to the lab to be dried at a temperature of 104°C. This was done to reduce moisture content which could affect the weight of the sample used for digestion. Samples were also crushed with a wooden mallet, wrapped in disposable parchment paper. An acid-washed mortar and pestle was used to further grind the samples to reduce subsample variability. The sample was thoroughly mixed, and a 1 g sample was weighed and recorded. The dry sample was transferred to a 100 mL Teflon microwave digestion tube. Next, 10 mL of (1+1) trace grade nitric acid was added to make a slurry in the test tube. Using a MARS 5 CEM microwave digester, the sample was gradually heated to 95°C over five minutes and allowed to reflux at that maintained temperature for five minutes. The sample was cooled for five minutes and then 5 mL of concentrated trace grade nitric acid was added. The sample was then gradually heated to 95°C and refluxed for 5 minutes. This step of adding 5 mL of concentrated Nitric acid was repeated until no brown fumes were formed indicating the complete reaction with the nitric acid. The sample was then gradually heated to 95°C and allowed to reflux for 10 minutes. Once the sample cooled for five minutes, 10 mL of 30% hydrogen peroxide was slowly added to prevent the sample from effervescing over the top of the sample. After the initial addition of hydrogen peroxide, 1 mL aliquots of hydrogen peroxide were added until the sample no longer effervesced, or the sample appeared unchanged. Next, the sample was gradually heated to 95°C over the course of 6 minutes and then maintained at 95°C without boiling for 10 minutes. After being allowed to cool, the remaining sample was diluted to 100 mL with DI water. Lastly, the sample was filtered with a 47 mm Whatman No. 41 filter with a pore size of 20-25 micrometers. Samples were stored in a refrigerator until sample analysis with an ICP-OES.

2.3.2. Laboratory Hardness Calculation

Hardness (in mg/L of $CaCO_3$) was calculated using calcium and magnesium concentrations measured using ICP-OES and using Equation 1 (Mallock, n.d.).

$$Hardness\ (\text{mg/L } CaCO_3) = (2.50 \times Ca) + (4.12 \times Mg) \quad (1)$$

Where:

Ca = Calcium Concentration (mg/L as Ca^{2+})

Mg = Magnesium Concentration (mg/L as Mg^{2+})

2.4. Laboratory Quality Control Measures

Laboratory quality control measures were developed to maintain a clean lab environment to avoid possible sources of contamination which would reduce the quality of data acquired. A thorough cleaning was done on all glassware used for sample digestion and analysis. All materials were washed with Dawn dish soap and rinsed with DI water and then washed with a 10% trace grade hydrochloric acid wash and then rinsed with DI water. All vials and test tubes used for sample analysis with the ICP-OES were disposed of after each use and not reused. All work areas including digestion, ICP-OES analysis, sample prep station were thoroughly washed with DI water and then a 5% nitric acid wash after each sample was processed. All laboratory prepared standards, digestion acid dilutions, and continues calibration standards were routinely remade to decrease the likelihood of cross-contamination.

2.4.1. Inductively Coupled Plasma Optical Emission Spectrometry

An inductively coupled plasma optical emission spectrometry (ICP-OES) was used to analyze metal concentrations in samples taken on Grove Gulch. An ICP-OES uses a plasma torch to burn a misted sample, which is then analyzed by optical emission spectrometry. The ICP-OES reads different emissions flares for the individual elements and records them in counts per second. Using known calibration standards made from multi-element stock solutions, calibration curves were developed which were used to calculate concentrations of individual elements in mg/L or parts per million (ppm) The ICP-OES was used for analysis because its detection limits for a wide variety of elements are less than 1 ppb. Another advantage of utilizing the ICP-OES for laboratory analysis is the high sample throughput allowing for fast turnaround time and increased control of sampling methods. The ICP-OES was used to analyze water, soil, and sediment samples that were taken from the Grove Gulch watershed.

2.4.2. Calibration Curve Development

The ICP-OES counts emission flares for different elements in counts per second. The purpose of developing a calibration curve with standards is to develop a curve that the ICP-OES software uses to correlate counts per second into concentrations in mg/L or ppm. For analysis, four calibration curve standards were created. Using Equation 2, a stock solution was made from a 100 µg/mL SPEX CertiPrep multi-element standard. Table V shows the volume of standard reagent used to make the different ppm calibration curve standards for the ICP-OES used for this thesis.

$$Standard\ Concentration\ \text{(ppm)} = \frac{V_1 \times C}{(V_T)} \qquad (2)$$

Where:

V_1 = Volume of Standard (mL)
C = Concentration of Standard (µg/mL)

V_T = Total volume of liquid added (Standard + Acid + DI Water)

Table V: Calibration Curve Standard Volumes

Calibration Curve Standard	Volume of 100 μg/mL multi-element standard (mL)	Volume of (1+1) Trace Grade Nitric Acid (mL)	Total Volume
50 ppb	0.05	2	100
0.5 ppm	0.5	2	100
1 ppm	1.0	2	100
5 ppm	5.0	2	100

2.4.3. Continuous Calibration Standards

Continuous calibration standards were prepared for the ICP-OES to determine the accuracy and quality control for the instrument. Three calibrations standards were created in order to provide quality control for the heavy metal analysis of the samples. Both multi-element standard stock solutions used to create calibration curve standards and continuous calibration standards are shown in Table VI. A 5 ppm solution was made from the SPEX CertiPrep multi-element standard and was used as the continuous calibration verification (CCV). Next, an initial calibration verification (ICV) was prepared by making a 10x solution by adding 5 mL of the TraceCERT multi-element standard to a 50 mL vial and topping off with DI water. The last continuous calibration standard was a continuous calibration blank (CCB) which was prepared by the addition of 2 mL of (1+1) trace grade nitric acid and filled with DI water in a 250 mL volumetric flask.

Table VI: Quality Control Multi-Element Standards

Product Company	Elements
SPEX CertiPrep Quality Control Standard 21	As, Be, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sr, Ti, Tl, V, Zn
TraceCERT Multi-Element Standard Solution	Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sr, Tl, Zn

2.4.4. Laboratory Duplicate

A laboratory duplicate was fortified in the lab to determine the spatial variance of a single sample for variances from laboratory equipment and digestion methods. The purpose of this quality control was to determine the effectiveness of the sampling equipment and digestion methods.

2.4.5. Laboratory Fortified Blank

A laboratory fortified blank (LFB) was used to determine whether the developed methodology was in control and the instrument was capable of making precise measurements. Another benefit of the LFB was it showed if any sample was cross contaminating from the prior analyzed sample and allowed invalidation of that sample run. The LFB was created from lab DI water and 2 mL of (1+1) trace metal grade nitric acid in a 250mL volumetric flask.

2.5. Data Processing

2.5.1. EPA Data

Prior data collected on Grove Gulch was acquired by USEPA Butte area project manager Nikia Greene. Data was collected by TREC, Inc. for the EPA and included samples from both base flow and stormwater sampling events. A total of 75 baseflow samples and 194 runoff/wet weather samples were obtained and analyzed to supplement the results section for this thesis.

Samples were collected from 2002 to 2017 and included water quality data, creek flow rates, and both TRM and TDM data for select heavy metals.

2.5.1.1. Loading Data and Flow Rates

Using the data provided by the EPA, heavy metal loading rates were calculated for the lower Grove Gulch section at the weir location. Using concentrations provided by the EPA in µg/L or ppb, flow rates in (L/day) and a conversion factor, loading rates were calculated in lb/day of heavy metals (shown in Equation 3). The concentration of heavy metals adsorbed onto the suspended sediments was calculated through the use of Equation 4.

$$Loading\ Rate\ \text{(lb/day)} = \frac{flow\ rate \times C}{453600000} \tag{3}$$

Where:

Flow Rate = L/day
C = Concentration of contaminate (µg/L)
453600000 = Conversion factor (µg to lb)

$$Fraction\ of\ Metals\ in\ TSS\ \text{(lb/day)} = TRM - TDM \tag{4}$$

Where:

TSS = Total Suspended Sediments Metal Loading Rate (lb/day)
TRM = Total Recoverable Metal loading rate (lb/day)
TDS = Total Dissolved Metal loading rate (lb/day)

2.5.2. MBMG Groundwater Information Center

The MBMG Groundwater Information Center (GWIC) is a central repository for information on the groundwater resources of Montana. Some of the information available from GWIC are well logs, water-level measurements, water quality reports, and other research projects. The main data acquired from GWIC for the use in this thesis were water-level measurements, well geospatial data, and water quality reports.

2.5.2.1. Surface Water Quality Data

Surface water quality was sampled by the MBMG from 1978 to 2011, along four locations on Grove Gulch. The four locations were at Rowe Road, Hanson Road, upstream of the landfill, and downstream of the landfill. The data was previously analyzed by Garrett Craig (Craig, 2016) and was obtained online from GWIC.

2.5.2.2. Potentiometric Water Table Characterization

Groundwater well data was obtained from MBMG's online GWIC for the Silver Bow Country. The resulting data set contained thousands of groundwater wells with partial information or information in the wrong location in the downloaded excel database. For this thesis, the data was separated into the different datums (NAD83, NAD27, WGS84) that were surveyed in. Next, any data missing latitude or longitude data were separated out of the data set. The well-log data sets were then imported into ArcGIS separately depending on the datums they were surveyed in. Using a pre-delineated watershed in GIS for Grove Gulch, only the groundwater wells located inside the watershed were selected. For wells missing elevation data, a digital elevation model was used to obtain well head elevation data. Using well head elevation data and static water level measurements, a static water level elevation was developed. The same was done to produce bottom of well casing elevations. Next, using static water elevation data, a raster was developed to produce potentiometric water level contours and 3D model diagrams to understand groundwater-surface water interactions for Grove Gulch.

3. Results

3.1. Land Use

Land use was characterized for the Grove Gulch watershed by using geospatial land use data acquired from the Montana State Library (Montana State Library, 2015). First, the land use data was imported into ArcGIS and added to the Grove Gulch watershed. Next, the individual types of land use categories were delineated in ArcGIS. There were multiple categories of different types of grasslands and wooded areas, and for simplicity, these categories were grouped together (Figure 11). Based off a watershed area of 7 mi^2, 20.6% is considered developed, 74.5% is considered undeveloped, and 4.9% is considered barren rock and water bodies (Figure 12).

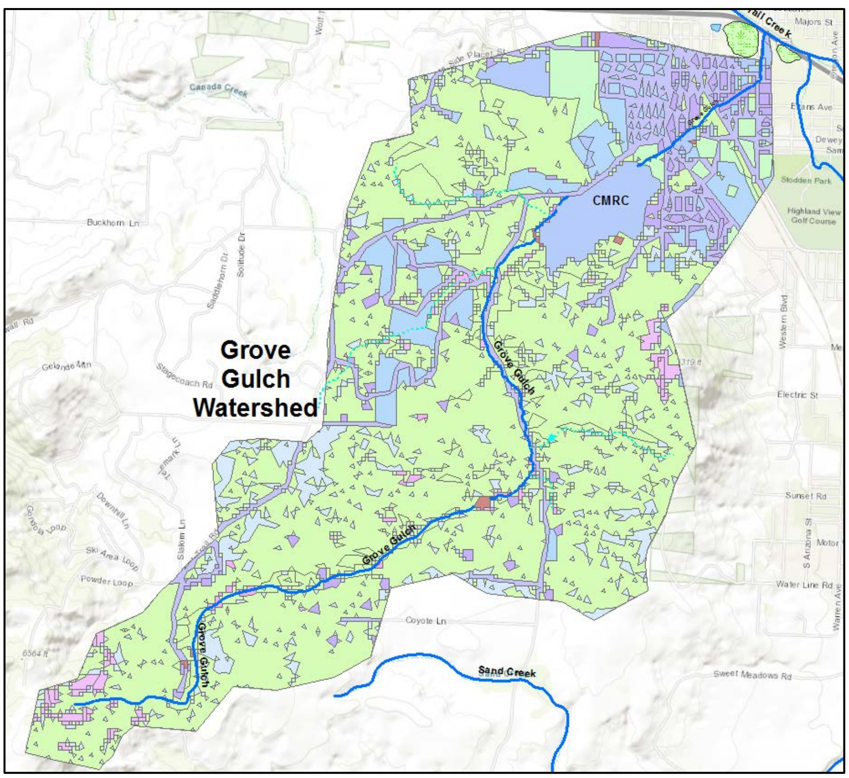

Figure 11: Grove Gulch watershed land use map

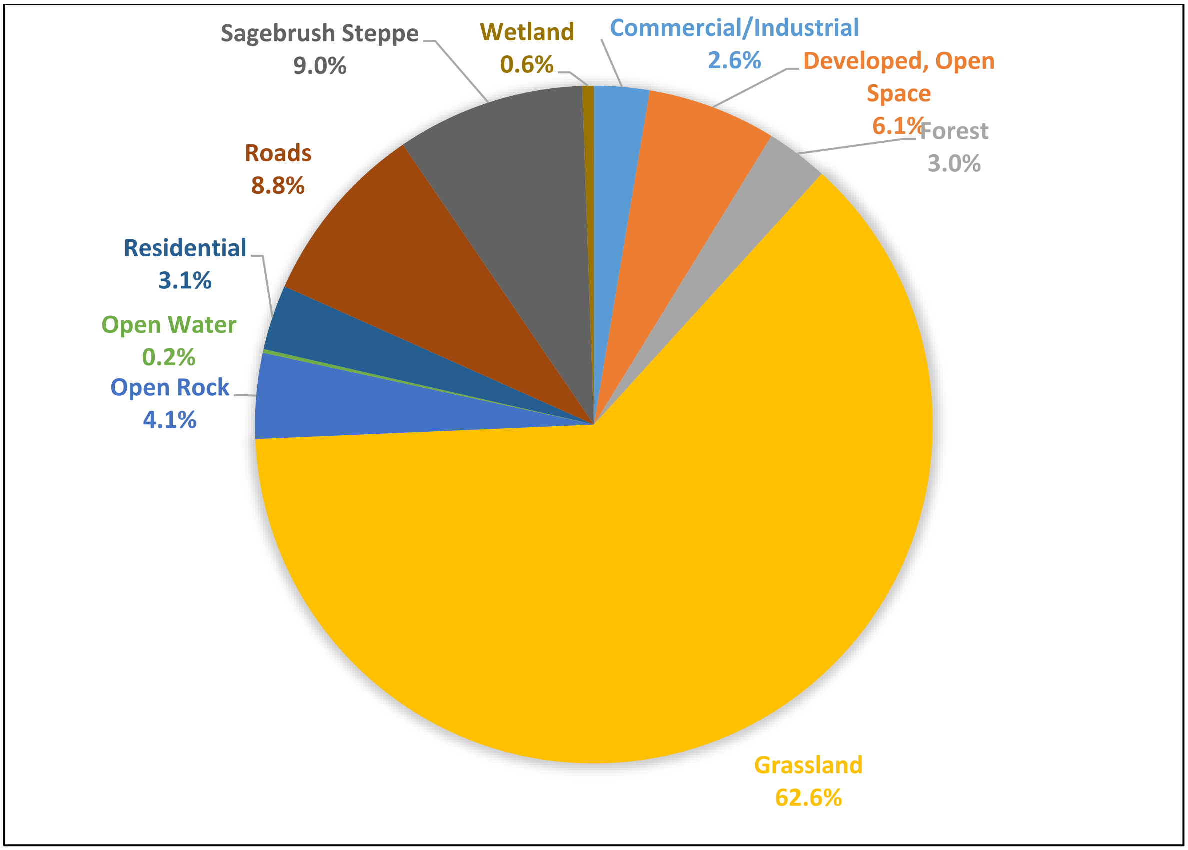

Figure 12: Grove Gulch watershed land use percentages

3.2. Hydrology

The hydrology of Grove Gulch is highly dependent on a combination of snowpack, precipitation, and groundwater. The main contribution to flow during normal high flow conditions is from annual snowmelt. The snowfall for Bert Mooney airport in 2017 was 62 inches (US Climate Data, 2018). Rainfall is the second source of surface water contribution which contributes to wet weather flow in Grove Gulch.

3.2.1. Flow Rate Calculations

Surface water flow rates were calculated by collecting surface water elevation data using a Solinst Levelogger and a man-made weir. Using collected water elevation data in Grove Gulch and a man-made weir located at GG-02 a flow rate was calculated using Equation 5. To be consistent with other data, flow rates were then converted from cubic meters per second to cubic feet per second. Flow measurements were calculated every fifteen minutes for a year and show normal high flow, wet weather flow, and base flow conditions when graphed (Figure 13). There is a strong correlation between increases in calculated flow rates and daily precipitation totals (Figure 14) (Weather Underground, 2018).

$$Flow\ Rate\ \left(\frac{m^3}{s}\right) = C \times L \times H^{\frac{3}{2}} \qquad \text{(NCEES, 2013)} \qquad (5)$$

Where:

C = 1.84 for rectangular weir (SI units)
L = Weir length (m)
H = Head (depth of discharge over weir) (m)

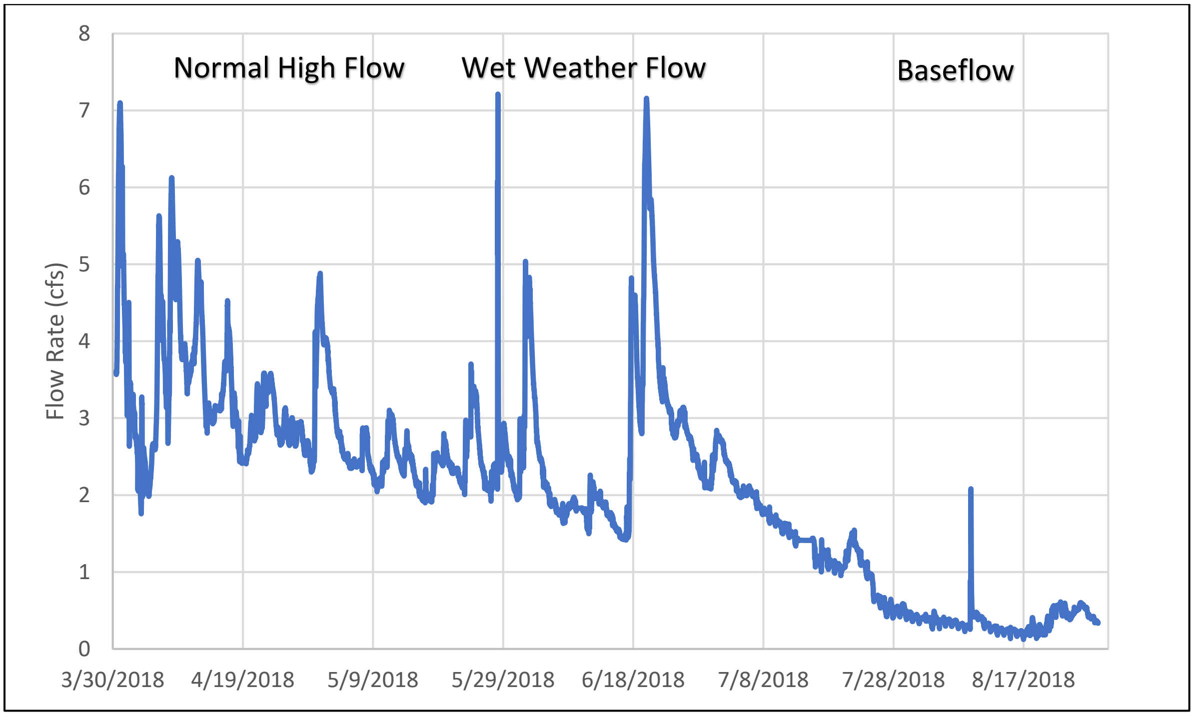

Figure 13: Calculated flow rates for weir location (GG-02)

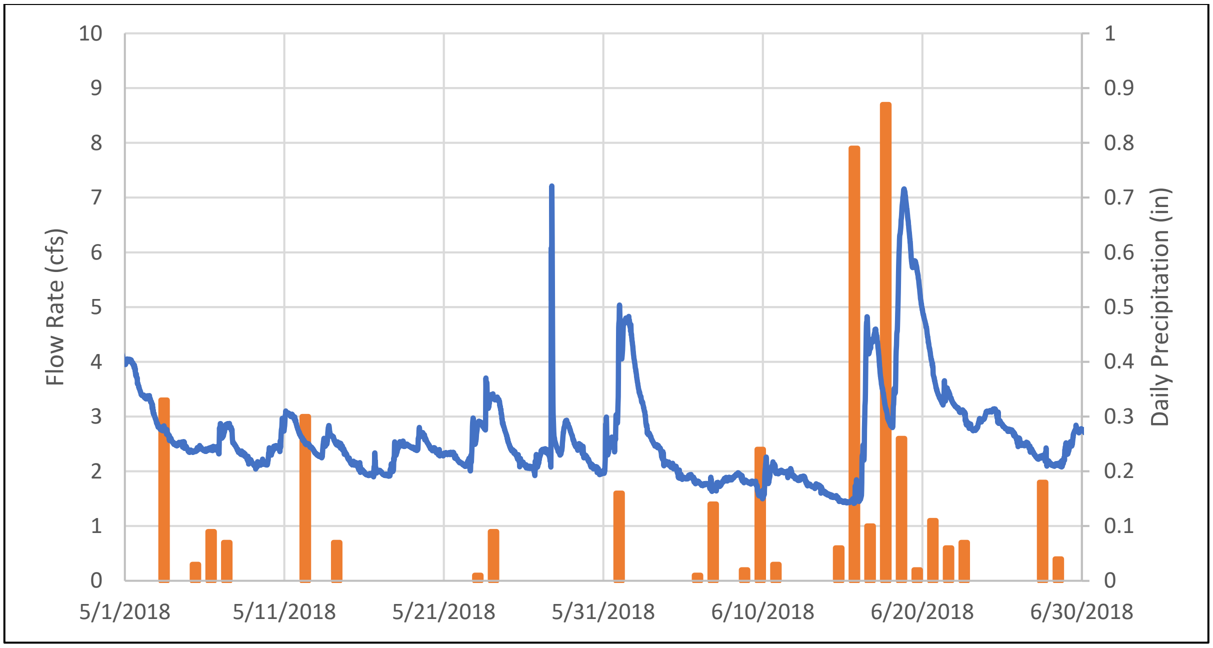

Figure 14: Flow rates in Grove Gulch compared with daily precipitation totals for May and June at GG-02

The flow rate was measured in the field for the concrete culvert (GG-06) and the downstream location (GG-05) in order to estimate the flow rate of the wooden culvert (GG-07). During a sampling event on 9/27/18, the flow rates for GG-05 were sampled with a Marsh McBirney Flowmaster 2000 and the concrete culvert (GG-06) was sampled with a bucket and timed. A water balance was conducted in order to determine the estimated flow for the wooden culvert (GG-07) (the flow balance was only an estimate and doesn't take into consideration groundwater contribution). The flow rate of the wooden culvert was calculated to be 0.35 cfs or about 51% of the total flow of the downstream location (GG-05). The calculations for both loading rates and water balance for each culvert and GG-05 are located in Appendix B. The zinc loading rate calculated for the concrete culvert (GG-06) was 0.024 lb/day, the wooden culvert (GG-07) was 3.96 lb.day, and the downstream location (GG-05) was 2.67 lb/day.

3.3. YSI Sonde Data

Two Multiparameter YSI EXO Sondes were utilized along Grove Gulch to continuously monitor water quality data. The two sondes were located at a downstream location (GG-02), and an upstream location (GG-08). The YSI sondes monitored data every 15 minutes for dissolved oxygen, temperature, pH, oxidation-reduction potential, conductivity, and turbidity. For pH, typical values ranged between 7-8 pH, conductivity measurements ranged from 100-2000 µS/cm, and turbidity measurements ranged from 0-60 Formazin Nephelometric Unit (FNU – from an infrared light source).

3.3.1. Dissolved oxygen

The dissolved oxygen (DO) relationship between the upstream and downstream sonde locations are shown in Figure 15. As expected, both the locations show daily variation in DO concentrations with lower values at night and higher concentrations during the day. The downstream sonde, located at sampling site GG-02, shows greater diurnal variation. The downstream sonde shows larger diurnal variation during base flow conditions in July (Figure 15). DO concentrations were also compared to water depth to determine the effect of groundwater influence on DO. When there was a drop in water depth there was also a corresponding drop in DO concentrations shown during the noon hours of 6/21, 6/23, and 6/29 (Figure 16) Aquatic plants stop producing oxygen at night, and produce more during daylight hours, the decrease in DO around noon could be from a decrease in surface water flow and more contribution from groundwater (which is deprived of DO).

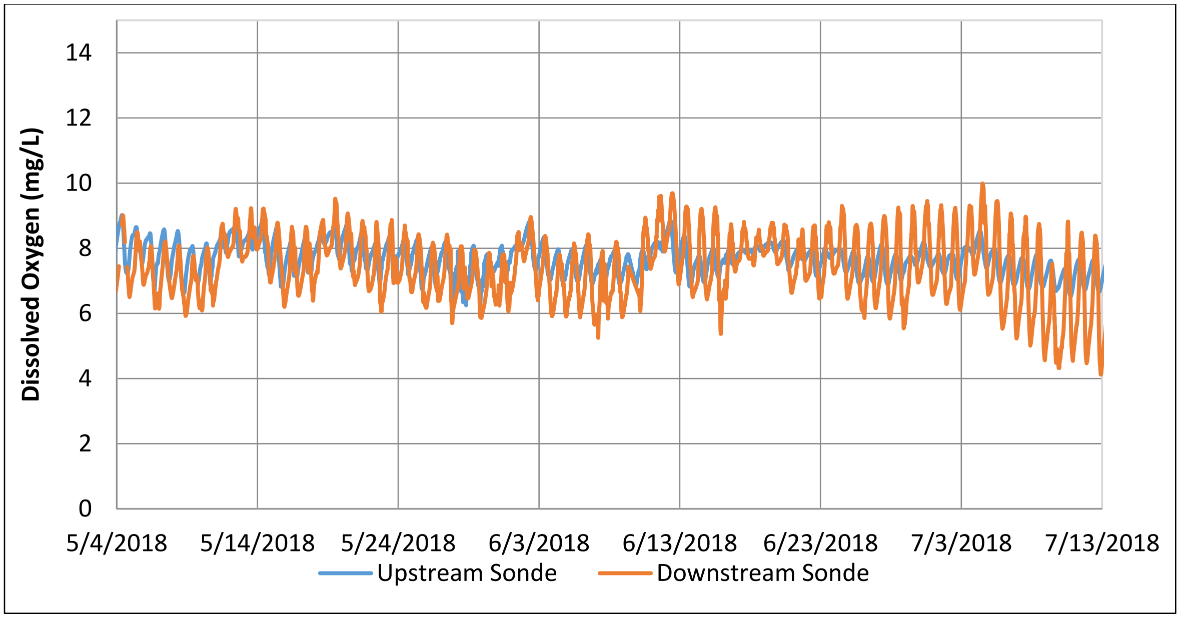

Figure 15: DO concentrations for upstream and downstream Sondes

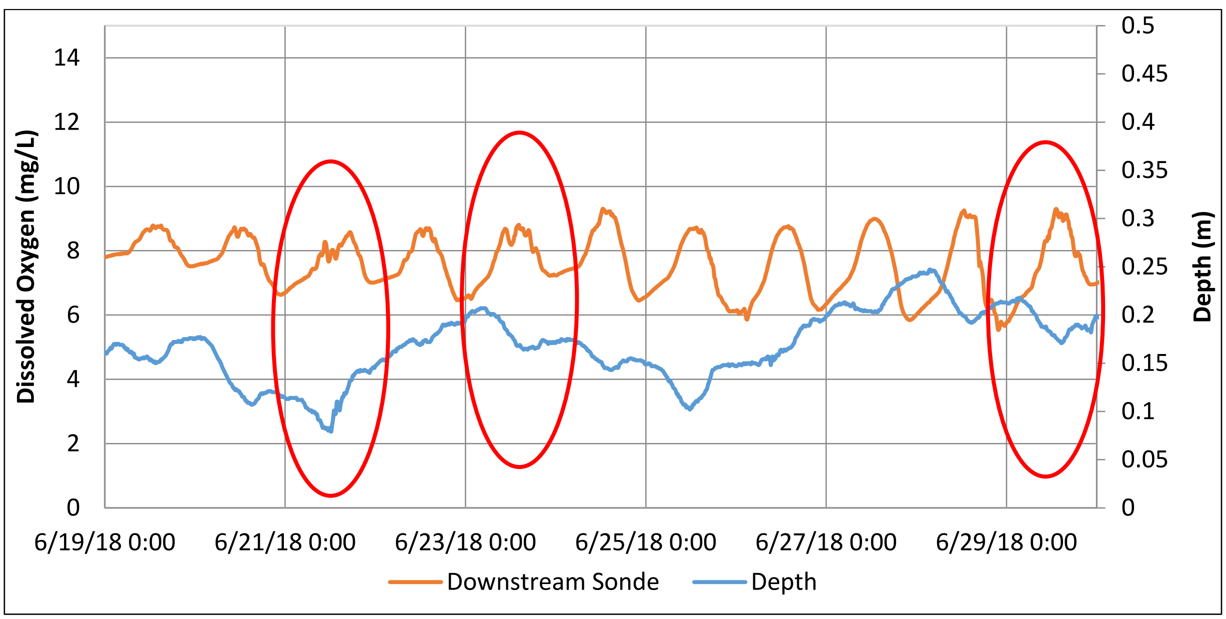

Figure 16: Dissolved oxygen compared to water depth

3.3.2. Turbidity

Turbidity is the measurement of how turbid, or cloudy, a water sample is. The turbidity for normal high flow conditions in both sondes ranges between 0 and 30 FNU (Figure 17).

Figure 17 also shows the difference between the upstream and the downstream sondes. Both the upstream and downstream sondes show correlating spikes in turbidity from wet weather events or increased flows, but the downstream sonde has relatively larger peaks in turbidity (Figure 17). The turbidity for base flow conditions ranges between 5 and 40 FNU for the upstream sonde and between 30 to 150 FNU for the downstream sonde (Figure 18).

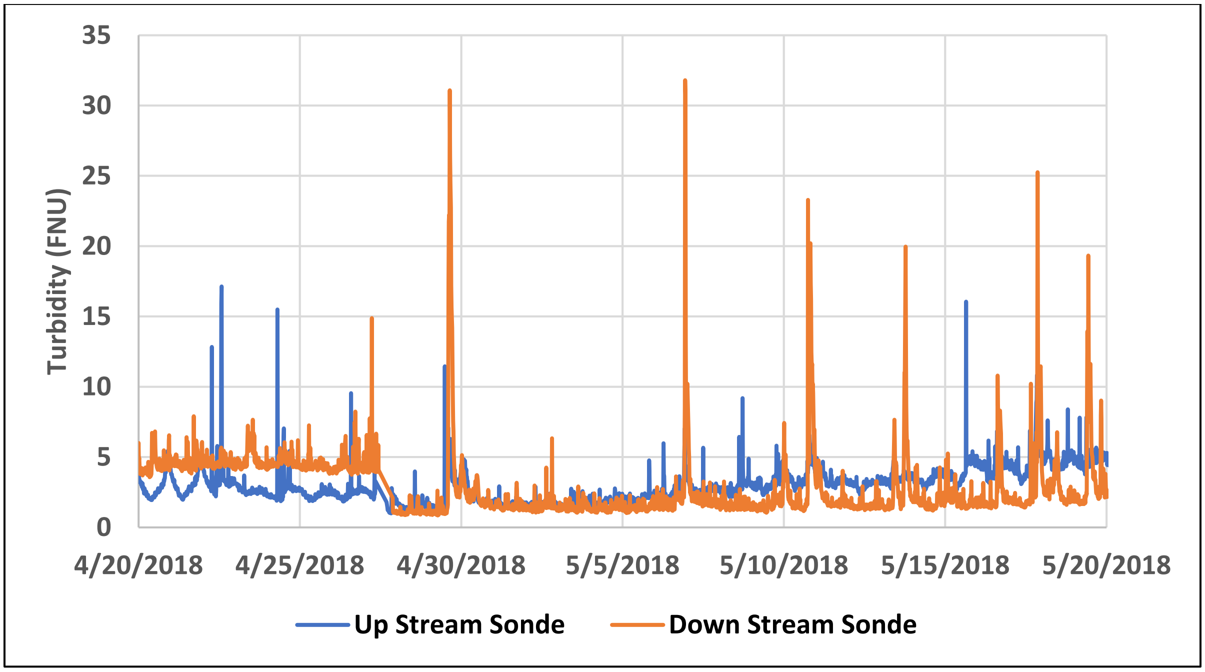

Figure 17: Turbidity concentrations for US and DS sondes during normal high flow conditions

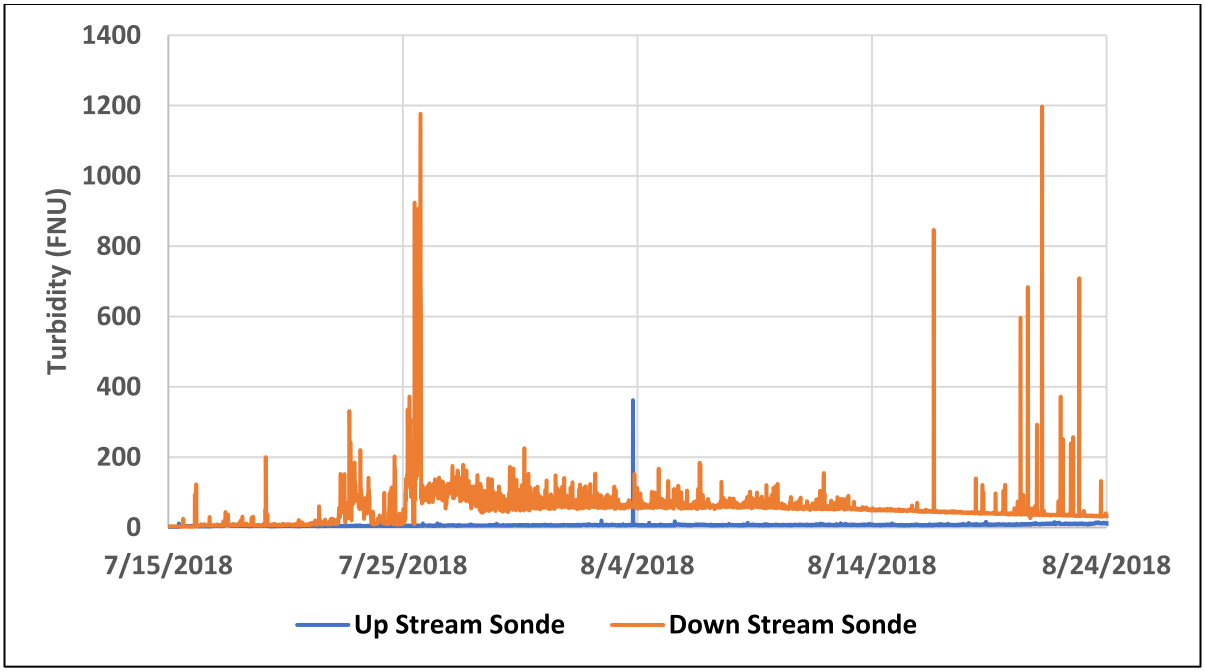

Figure 18: Turbidity concentrations for US and DS sondes during base flow conditions

The turbidity data also corresponded with flow data, which was acquired from a level logger and used with a weir to calculate flow. This correlation shows that there is an increase in turbidity from precipitation events (Figure 19). On 6/16/18 and 6/18/18 two wet weather events occurred producing an average precipitation of 0.79 inches and 0.87 inches which also corresponds to peaks in turbidity and flow rate (Figure 19) (Weather Underground, 2018). A wet weather event on 8/13/17 shows the average baseflow values (shown as straight lines) and plotted runoff values for turbidity and specific conductivity. During wet weather flow, there is a strong correlation between increased values for turbidity and specific conductivity over the average base flow conditions from a wet weather event (Figure 20).

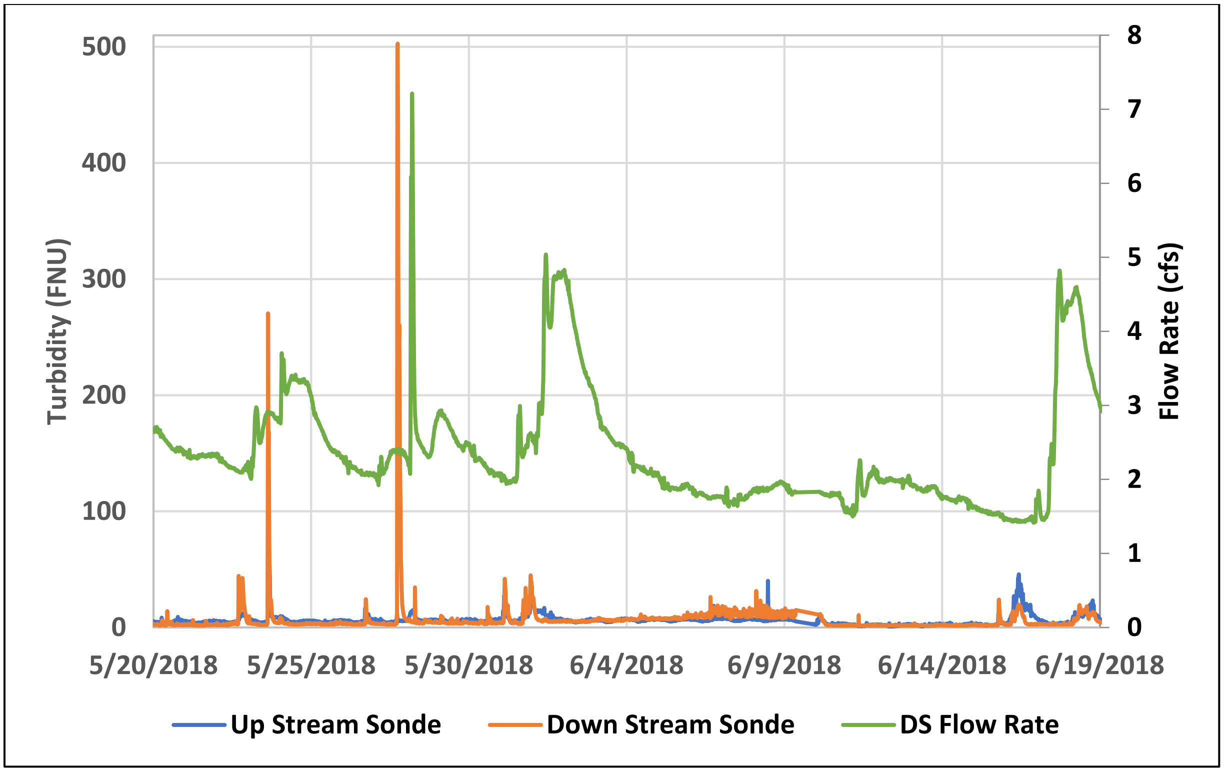

Figure 19: Turbidity concentrations for US and DS sondes during precipitation events 5/20/18 to 6/5/18

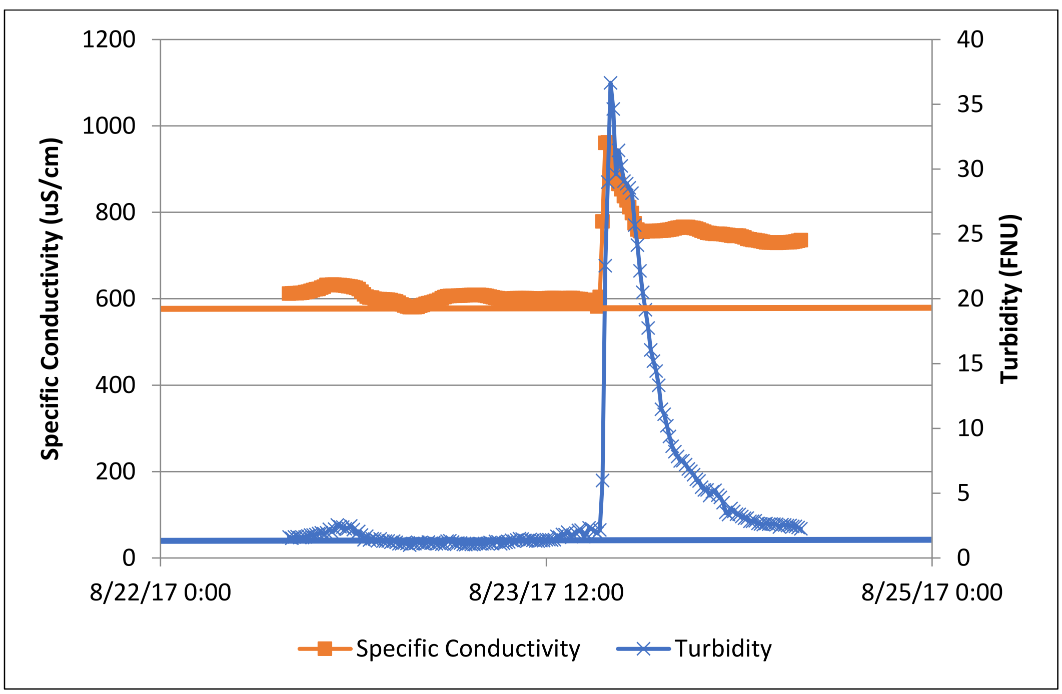

Figure 20: Baseflow vs precipitation event on 8/13/117 for turbidity and specific conductivity

3.3.1. Total Suspended Sediments Loading Data

Total suspended sediment (TSS) loading data was calculated by using field turbidity data from the downstream sonde. A regression equation was developed to estimate suspended solids concentrations given the turbidity concentrations. In order to calculate TSS from turbidity data, a laboratory experiment was conducted to determine the correlation between the two variables (Becker, n.d.). Grove Gulch water was taken from the creek and allowed to settle overnight in a bucket. Samples were then taken from the bucket at different intervals after mixing in soil/sediment material (material was compiled from sediment samples from Grove Gulch). The water samples were then filtered and weighed to determine the TSS in each sample. The samples were also measured for turbidity. The resulting experiment produced a regression equation (Equation 6) that could be used to calculate TSS in mg/L from turbidity measurements from the sonde (Figure 21).

$$Total\ Suspended\ Sediments\ (\mathrm{mg/L}) = 3.8033\ (Turbidity\ (FNU)) \tag{6}$$

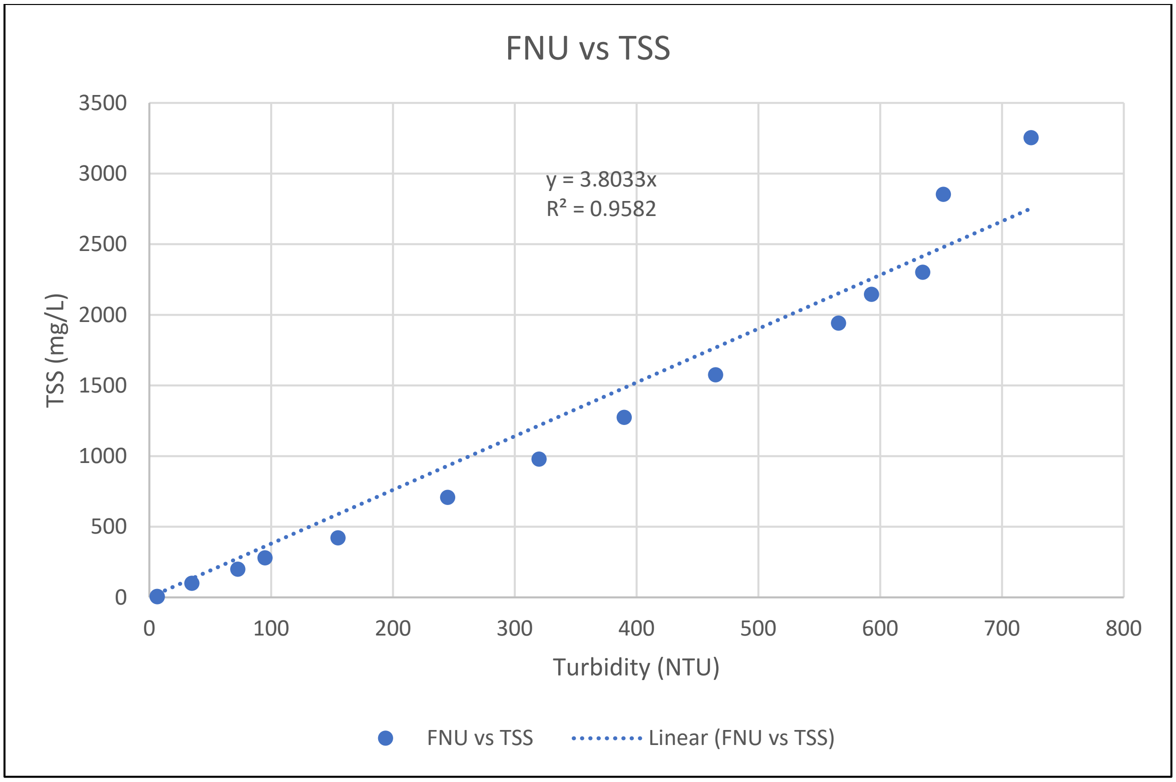

Figure 21: Correlation Between TSS and Turbidity

TSS loading rates were calculated by using TSS (mg/L) calculated from Equation 4 and flow data acquired from the field into Equation 7. Using the calculated TSS loading rates, zinc loading rates were calculated by using a minimum, maximum and average sediment zinc concentration from 24 sediment samples from Grove Gulch. The minimum concentration used for zinc was 96.9 mg/kg, the maximum concentration used was 5482 mg/kg, and the average concentration used was 1625.7 mg/kg. Zinc loading rates were calculated using sonde turbidity data at fifteen-minute intervals. The zinc loading rates (using the average zinc concentration) were compared with the flow rate from 3/30/18 to 8/28/18 (Figure 22). From May to late June the average loading rates for zinc were consistent around 0.2 – 1.0 lb/day with some spikes from wet weather events. From late July to August, baseflow conditions had lower flow rates but higher turbidity values causing loading rates for zinc to fluctuate and ranged around 0.6 – 2 lb/day (Figure 22). Using the calculated loading rate, a cumulative zinc load was estimated from sediments based off of turbidity data in Grove Gulch (Figure 23). The estimated minimum load of zinc being transported via TSS was 4.48 lb, the maximum was 253.6 lb of zinc, and the average was 75.2 lb of zinc. Additional figures for the other calculated zinc loading rates and cumulative load are found in Appendix A.

$$Loading\ Rate\ (lb/day) = TSS\ \left(\frac{mg}{L}\right) *\ MGD * 8.34 \tag{7}$$

Where:

TSS = Total Suspended Sediments
MGD = Million Gallons per Day = (flow rate (cfs) * 0.5381)
8.34 = Conversion factor

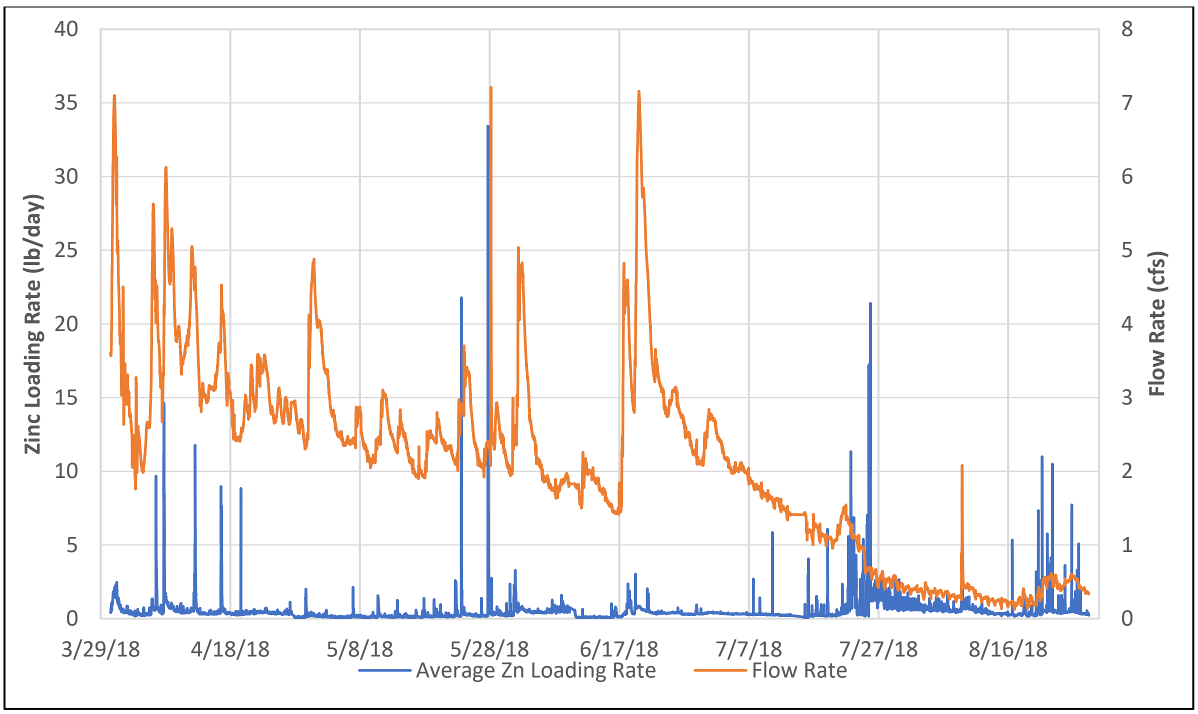

Figure 22: Flow rate vs calculated average zinc loading rates for GG-02

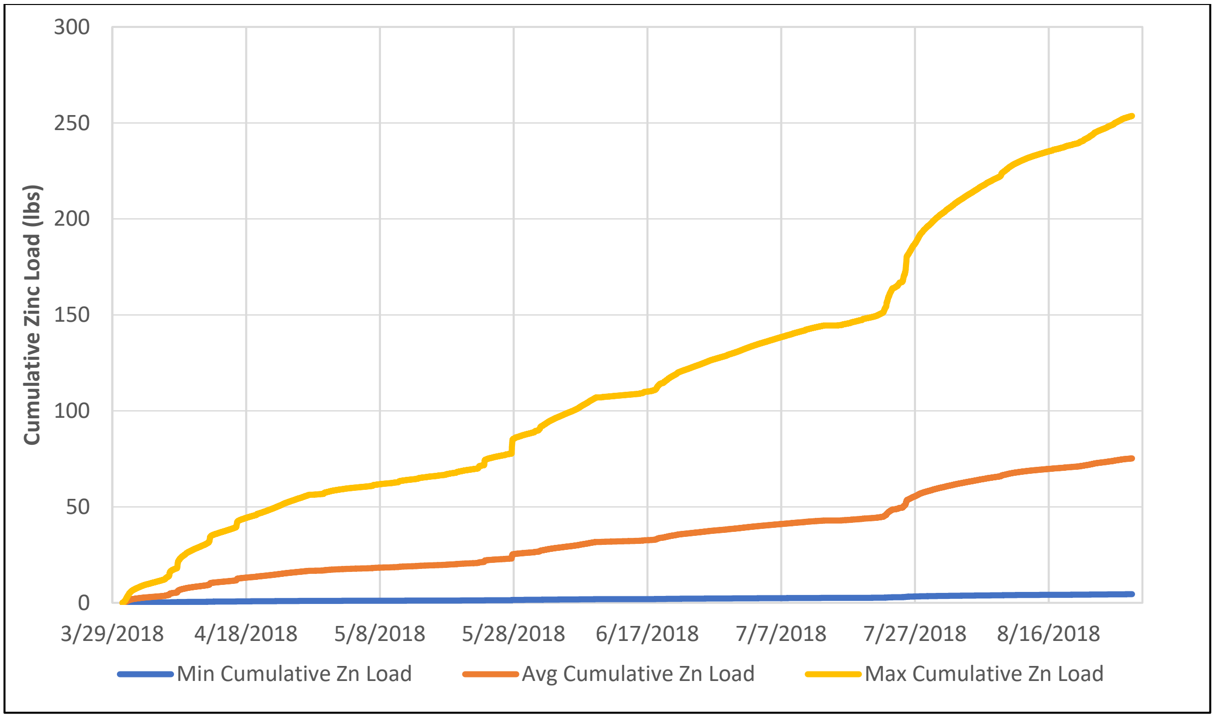

Figure 23: Cumulative zinc load for the minimum, average and maximum sampled sediment concentrations

3.4. Heavy Metal Analysis for Grove Gulch Creek Water

Heavy metals are transported in Grove Gulch in two phases, the first being in the dissolved phase that is smaller than 0.45 microns, and the second is in the adsorbed phase (adsorbed to particles larger than 0.45 microns). Total recoverable metals (TRM) include both the dissolved and undissolved fraction of heavy metals; total dissolved metals (TDM) include only the dissolved fraction. In order to understand what fraction makes up the concentrations of heavy metals in Grove Gulch, both TRM and TDM were analyzed to understand the speciation of the heavy metals. In order to understand the impact of the wooden culvert on Grove Gulch, extensive sampling was conducted on the wooden culvert and the surrounding area.

3.4.1. Dissolved Vs Particulate Concentration Analysis

In order to quantify the concentration of heavy metals adsorbed onto the particulate fraction of a water sample, the relationship between TRM and TDM must be compared. Four locations were picked to show the relationship between dissolved and particulate concentrations of heavy metals. The three sampling locations near the wooden culvert (GG-07, GG-06, and GG-05) were analyzed to show the effect of the wooden culvert (GG-07) on the rest of Grove Gulch. The fourth sample location was GG-01 which is the last sampling point before Grove Gulch flows into BTC. The concrete culvert contains trace levels of heavy metals, while the downstream Grove Gulch sampling point (GG-05) shows elevated levels of heavy metals originating from the wooden culvert (GG-07). Figures 24 – 28 show four sampling events, 11/17/17 and 12/11/17 are base flow events, 5/18/18 was a wet weather event, and lastly, 6/5/18 was a normal high flow sampling event. Samples that were below the LDL for the ICP-OES are represented by blank bars on the graphs in Figures 24 to 28.

3.4.1.1. Arsenic

The arsenic sampled in Grove Gulch was contained primarily in the dissolved phase with some samples containing more in the undissolved phase. The wooden culvert (GG-07) discharged mostly arsenic in the dissolved phase (Figure 24). The lower detection limit (LDL) for arsenic was 2.14 ppb and a majority of the other samples were at or around the LDL when comparing TRM and TDM.

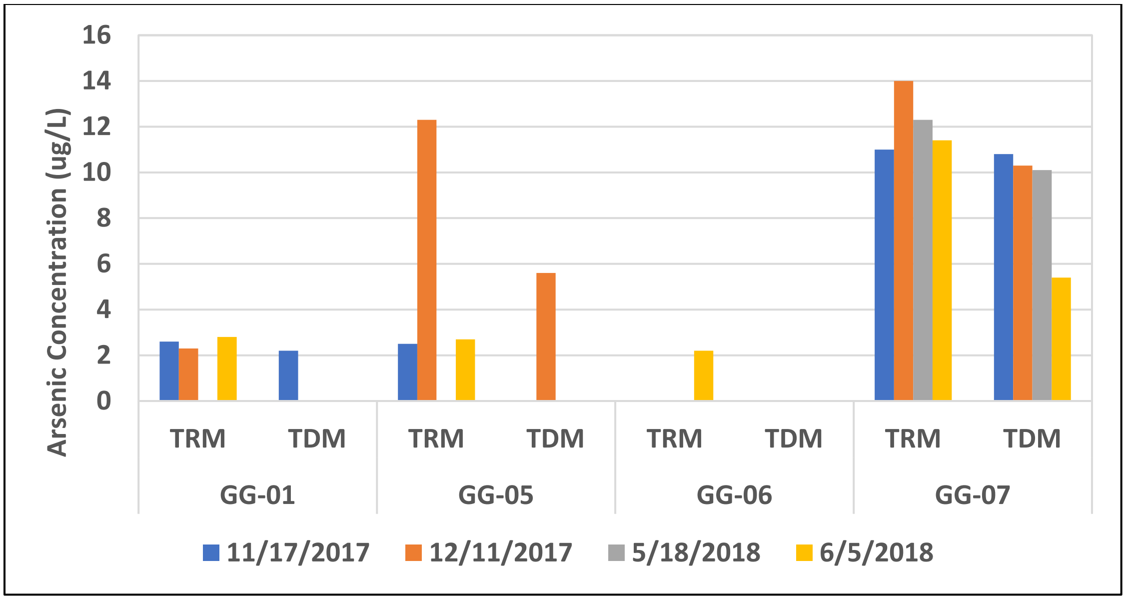

Figure 24: Arsenic TRM vs TDM

3.4.1.2. Copper

For copper, it was hard to differentiate between TRM and TDM, and one reason was that a majority of the initial samples contained copper concentrations levels that were below the LDL of 0.39 ppb (Figure 25). Later in the year sampling of copper levels were elevated above the LDL but the dissolved fraction was not analyzed and only TRM concentrations were analyzed.

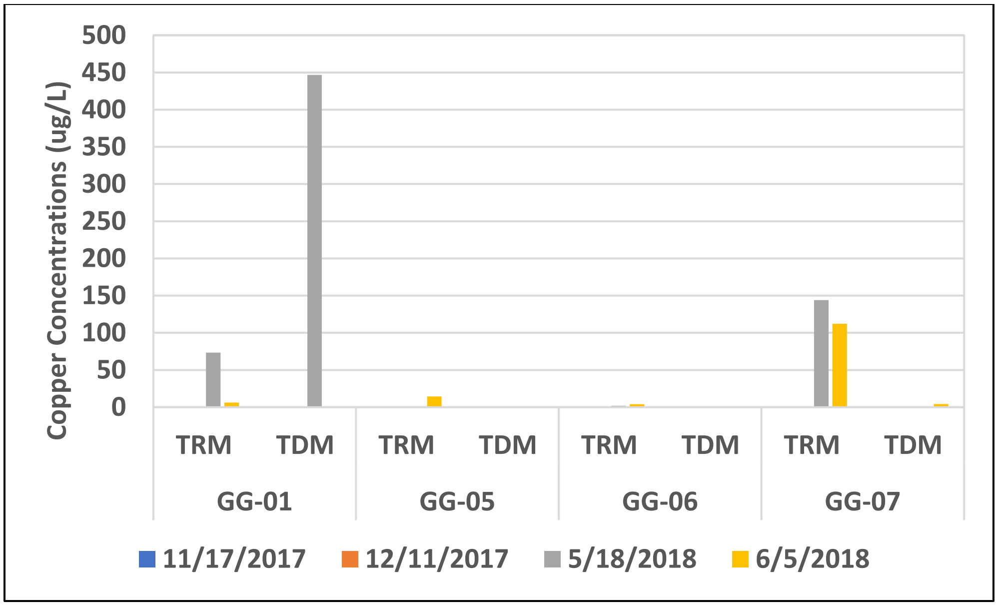

Figure 25: Copper TRM vs TDM

3.4.1.3. Iron

For Iron, the majority of baseflow samples contained more of the dissolved fraction of the metals then undissolved (Figure 26). Iron was visually deposited on the streambed in and around the wooden culvert, which was characterized by orange precipitated iron buildup in mats around the culvert and along Grove Gulch (Figure 4). Samples taken on 12/11/17, 5/18/18 and 6/5/18 contain larger fractions of undissolved iron, specifically in GG-05 and GG-07 (Figure 26).

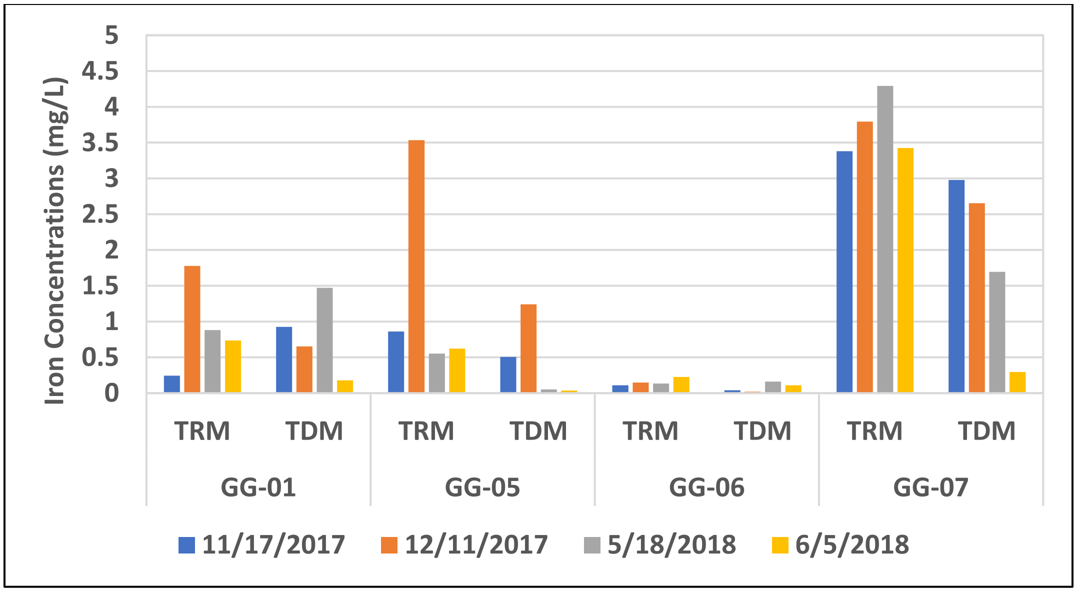

Figure 26: Iron TRM vs TDM

3.4.1.4. Lead

The base flow samples contained mostly dissolved concentrations of lead. The normal high and wet weather flow events contained larger concentrations of lead in the undissolved phase (Figure 27). Some samples for lead were near the LDL of the ICP-OES at 1.06 ppb, shown by a black space on the graph. During the sampling event on 6/18/18, the TRM maximum lead concentrations at the trailer park (GG-03) was 1,892 ppb while only 1.2 ppb was TDM. The larger concentration of TRM compared to TDM is explained by increased lead-laden particulates from runoff events during a wet weather event on 6/18/18.

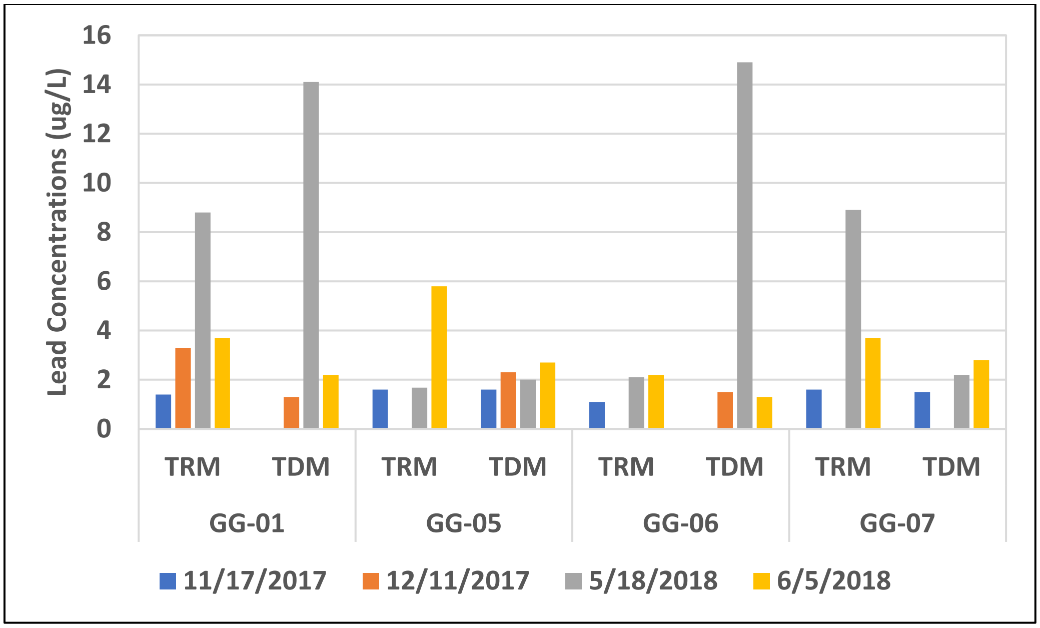

Figure 27: Lead TRM vs TDM

3.4.1.5. Zinc

Zinc was mostly transported in the surface water in the dissolved form for both base flow and normal high flow conditions, which is shown by the comparison of TRM and TDM of the zinc (Figure 28). For the precipitation event on 5/18/18, higher TRM concentrations compared to the dissolved fraction (TDM) show that more zinc-laden particulates, which can be from disturbed creek bed sediments or surface runoff, impacted that sampling event.

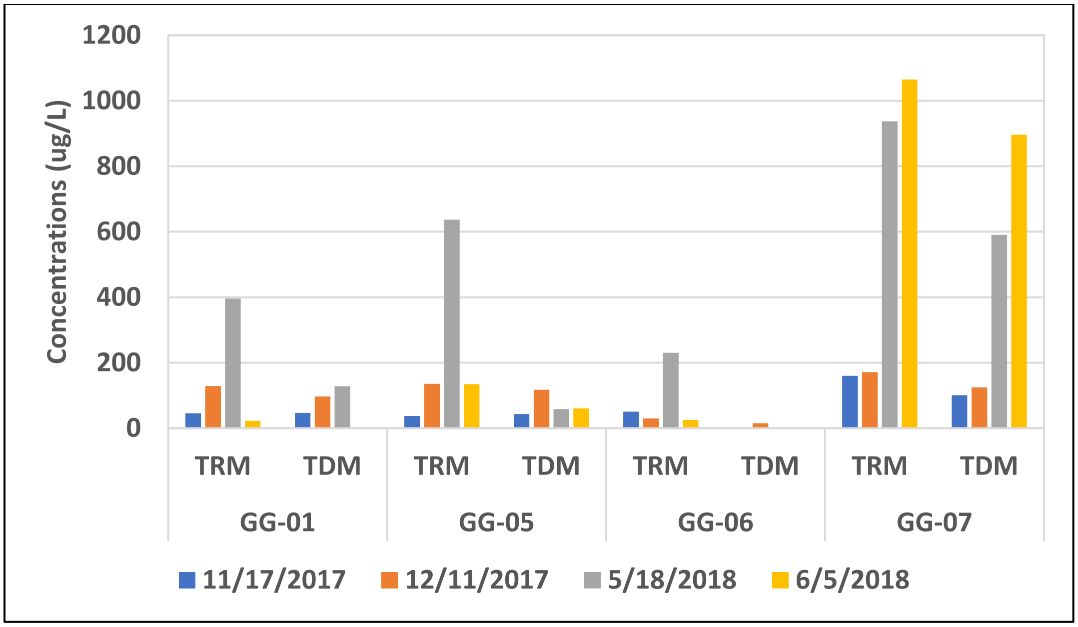

Figure 28: Zinc TRM vs TDM

3.4.2. Heavy Metal Water Quality Exceedances

Heavy metal standards for water bodies in the State of Montana are propagated by the Circular DEQ - 7 Montana Numeric Water Quality Standards for aquatic life, while human health standards are also defined by the EPA maximum contaminate level (MCL). Montana aquatic life standards are split between acute and chronic standards, where acute standards govern normal high flow and wet weather flow conditions while chronic standards govern base flow conditions (MTDEQ, 2012; USEPA, 2009). The wooden culvert (GG-07) is a source to Grove Gulch Creek, and not part of Grove Gulch. The wooden culvert (GG-07) is not applicable to human health standards and MTDEQ Circular -7 standards but is compared with the other Grove Gulch samples to show the extent of heavy metal concentrations present. Specific water quality exceedances for the different heavy metals in Grove Gulch, specifically for each sampling location, are discussed in the following sections (3.4.2.1 to 3.4.2.6).

3.4.2.1. Arsenic

The arsenic standards for Grove Gulch are set by the MCL human health standard of 10 ppb (USEPA, 2009). Samples were only compared to the human health standard MCL for arsenic because no arsenic samples exceeded the MTDEQ aquatic life standards. For elevated flow conditions, the wooden culvert (GG-07) exceeded 100% of the samples taken, while the downstream location (GG-05), after the two culverts mix, exceeded 29% of the samples for arsenic (Table VII).

Table VII: Arsenic Maximum Contaminate Level Water Quality Exceedances for Elevated Flow Conditions

Site Name	n	Minimum (μg/L)	Maximum (μg/L)	Number of Exceedances	Percent of Exceedances
GG-01	7	2.7	5.4	0	0%
GG-02	0	--	--	0	0%
GG-03	5	<2.14	4.8	0	0%
GG-04	5	2.5	4.5	0	0%
GG-05	7	2.7	14.3	2	29%
GG-06	3	2.2	4.7	0	0%
GG-07	5	11.4	29.4	5	100%
GG-08	0	--	--	0	0%
GG-10	7	3.4	5.3	0	0%
BTC-US	2	<2.14	2.3	0	0%
BTC-VC	2	<2.14	2.8	0	0%

For base flow conditions, the wooden culvert (GG-07) 5 of 7 samples, or 71% exceeded, while the downstream location (GG-05) roughly 43% of the samples exceeded the human health standard for arsenic (Table VIII). Specifically, the max concentration for the wooden culvert measured at 31.6 ppb, although not applicable to the standards set by the EPA and MTDEQ, is still three times the human health standard for arsenic.

Table VIII: Arsenic Maximum Contaminate Level Water Quality Exceedances for Base Flow Conditions

Site Name	n	Minimum (μg/L)	Maximum (μg/L)	Number of Exceedances	Percent of Exceedances
GG-01	5	2.3	3.6	0	0%
GG-02	2	3.1	4.3	0	0%
GG-03	4	2.4	3	0	0%
GG-04	5	<2.14	9.6	0	0%
GG-05	7	2.5	12.3	3	43%
GG-06	6	4.7	4.9	0	0%
GG-07	7	6.3	31.6	5	71%
GG-08	2	<2.14	<2.14	0	0%
GG-10	3	<2.14	3.1	0	0%
BTC-US	0	--	--	0	0%
BTC-VC	0	--	--	0	0%

3.4.2.2. Cadmium

Cadmium for normal high or wet weather conditions did not have any acute aquatic life standard exceedances. During base flow conditions cadmium exceeded chronic aquatic life standards for 29% of samples taken at the wooden culvert (GG-07) (Table IX). The concrete culvert (GG-06) which connects upstream and downstream Grove Gulch did not exceed any chronic aquatic life standards. Table IX also shows that the mixing point downstream of the two culverts (GG-05) 43% of the samples taken for cadmium exceeded and the Hanson Road sampling location (GG-04) 25% of the samples exceed for cadmium.

Table IX: Chronic Cadmium Water Quality Exceedances

Site Name	n	Minimum (µg/L)	Maximum (µg/L)	Number of Exceedances	Percent of Exceedances
GG-01	5	0.1	0.5	0	0%
GG-02	2	<0	<0	0	0%
GG-03	4	0.1	0.3	0	0%
GG-04	4	0.1	0.4	1	25%
GG-05	7	0.5	0.9	3	43%
GG-06	6	<0	0.1	0	0%
GG-07	7	0.1	1.7	2	29%
GG-08	2	<0	<0	0	0%
GG-10	3	<0	0.2	0	0%
BTC-US	0	--	--	0	0%
BTC-VC	0	--	--	0	0%

3.4.2.3. Copper

Copper concentration analysis showed exceedances for acute and chronic aquatic life standards for sampling along Grove Gulch. Specifically, in table X the wooden culvert shows that 40% of the samples exceed the acute standards with the maximum sampled value of 143.9 ppb. The maximum concentration measured was six times the hardness adjusted standard of 23.8 ppb. The water samples that were taken along Grove Gulch in the trailer court (GG-03), 60% of the samples exceed for copper, with the maximum sample concentration being over fifteen times the hardness adjusted standard of 17.7 ppb. For chronic conditions, 18% of samples exceeded the chronic aquatic life standard for baseflow conditions (Table XI). The downstream combination location (GG-05) had a maximum concentration for copper of 152.2 ppb which is eleven times the hardness adjusted standard of 13.5 ppb.

Table X: Acute Copper Water Quality Exceedances

Site Name	n	Minimum (µg/L)	Maximum (µg/L)	Number of Exceedances	Percent of Exceedances
GG-01	7	0.8	87.4	2	29%
GG-02	0	--	--	0	0%
GG-03	5	54.6	268.6	3	60%
GG-04	6	4.5	48.8	2	33%
GG-05	7	2.5	115.2	1	14%
GG-06	3	1.9	4	0	0%
GG-07	5	0.8	143.9	2	40%
GG-08	0	--	--	0	0%
GG-10	7	0.9	1.9	0	0%
BTC-US	2	6.4	7.7	0	0%
BTC-VC	2	1.4	6.2	0	0%

Table XI: Chronic Copper Water Quality Exceedances

Site Name	n	Minimum (µg/L)	Maximum (µg/L)	Number of Exceedances	Percent of Exceedances
GG-01	5	9	20.2	1	20%
GG-02	2	<0.39	<0.39	0	0%
GG-03	4	11	21	1	25%
GG-04	5	7.6	10.6	0	0%
GG-05	7	5.8	152.6	2	29%
GG-06	6	8.2	13.9	1	17%
GG-07	7	8.3	37.1	1	14%
GG-08	2	<0.39	<0.39	0	0%
GG-10	0	3	25.4	1	0%
BTC-US	0	--	--	0	0%
BTC-VC	0	--	--	0	0%

3.4.2.4. Iron

For iron, the MTDEQ Circular – 7 establishes a chronic aquatic life standard at 1 ppm which only applies to base flow sampling events. For chronic exceedances, Table XII lists each sampling location and the number of samples exceeding the chronic standard of 1 ppm. The wooden culvert (GG-07), 100% of the samples exceed for iron, with the maximum sample over eight times the chronic standard. The downstream location (GG-05), 67% of the sample exceed iron, with all but one of the samples over three times the standard of 1 ppm.

Table XII: Chronic Iron Water Quality Exceedances

Site Name	n	Minimum (mg/L)	Maximum (mg/L)	Number of Exceedances	Percent of Exceedances
GG-01	5	0.1681	1.7780	1	20%
GG-02	2	0.9830	2.2400	1	50%
GG-03	4	0.1178	0.6131	0	0%
GG-04	5	0.2960	5.3460	1	20%
GG-05	6	0.8608	3.6990	4	67%
GG-06	4	0.1107	0.1714	0	0%
GG-07	6	3.2520	8.4480	6	100%
GG-08	2	0.1236	0.2116	0	0%
GG-10	3	0.1505	0.2939	0	0%
BTC-US	0	--	--	0	0%
BTC-VC	0	--	--	0	0%

3.4.2.5. Lead

For lead, both human health standards and MTDEQ aquatic life standards apply to samples taken from Grove Gulch. The human health MCL standard for lead is 15 ppb (USEPA, 2009). The only acute exceedance location for lead was at the trailer park (GG-03) where 1 of 5 samples exceeded the acute aquatic life standard and 2 of 5 samples exceeded the human health standard (Table XIII). During a normal high flow sampling event, the lead was measured at 1892 ppb which was 16.9 times the hardness adjusted standard of 111.9 ppb for the trailer park location (GG-03). For base flow conditions, the Hanson Road (GG-04), trailer park (GG-03) and the weir location (GG-02) all had chronic exceedances for lead (Table XIV). Lastly, only GG-04 had an exceedance for lead for the human health standard of 15 ppb.

Table XIII: Acute and MCL Lead Water Quality Exceedances

Site Name	n	Minimum (µg/L)	Minimum (µg/L)	Number of Exceedances	Percent of Exceedances	MCL	MCL %
GG-01	7	3.00	8.80	0	0%	0	0%
GG-02	0	--	--	0	0%	0	0%
GG-03	5	2.70	1892.00	1	37%	2	40%
GG-04	5	2.20	6.80	0	0%	0	0%
GG-05	7	1.68	10.30	0	0%	0	0%
GG-06	3	2.10	2.20	0	0%	0	0%
GG-07	5	1.50	8.90	0	0%	0	0%
GG-08	0	--	--	0	0%	0	0%
GG-10	7	1.90	4.30	0	0%	0	0%
BTC-US	2	3.40	3.40	0	0%	0	0%
BTC-VC	2	3.40	3.70	0	0%	0	0%

Table XIV: Chronic and MCL Lead Water Quality Exceedances

Site Name	n	Minimum (µg/L)	Minimum (µg/L)	Number of Exceedances	Percent of Exceedances	MCL	MCL %
GG-01	5	1.40	6.50	0	0%	0	0%
GG-02	2	3.50	12.40	1	50%	0	0%
GG-03	4	3.30	15.70	1	25%	0	0%
GG-04	5	1.20	36.60	1	20%	1	20%
GG-05	7	1.10	6.00	0	0%	0	0%
GG-06	6	1.10	2.70	0	0%	0	0%
GG-07	7	1.40	6.80	0	0%	0	0%
GG-08	2	2.10	2.10	0	0%	0	0%
GG-10	3	2.30	5.10	0	0%	0	0%
BTC-US	0	--	--	0	0%	0	0%
BTC-VC	0	--	--	0	0%	0	0%

3.4.2.6. Zinc

Grove Gulch is the historic location of the Timber Butte Zinc Mill and based off of sampling analysis and the number of exceedances, zinc is the most prevalent of the heavy metals in the surface water. The human health standard for zinc set by the EPA MCL is 2,000 ppb (USEPA, 2009). For the wooden culvert (GG-07), 6 of 12 samples exceed the human health standard for zinc or 50%. The downstream location (GG-05), had 1 of 14 samples exceed the human health standard for zinc or 7% (Table XV). In total, 50% of all normal high flow and wet weather flow samples exceeded acute aquatic life standards (Table XVI). The wooden culvert (GG-07) and Hanson Road (GG-04), a 100% of the samples exceed zinc for acute standards. The downstream combined location (GG-05), 71% of the samples exceed with the maximum concentration of 1999 ppb over seven times the hardness adjusted standard of 257.8 ppb. The maximum concentration for zinc of 3901 ppb from the wooden culver (GG-07) was thirteen times the hardness adjusted standard of 299.9 ppb.

Table XV: Zinc Human Health Water Quality Exceedances

Site Name	n	Minimum (µg/L)	Minimum (µg/L)	Number of Exceedances	Percent of Exceedances
GG-01	12	36.9	396.0	0	0%
GG-02	2	63.3	238.7	0	0%
GG-03	9	32.1	1051.0	0	0%
GG-04	10	36.8	1200.0	0	0%
GG-05	14	37.3	2294.0	1	7%
GG-06	9	9.1	230.5	0	0%
GG-07	12	134.7	3901.0	6	50%
GG-08	2	2.5	193.3	0	0%
GG-10	7	4.3	37.6	0	0%
BTC-US	2	14.8	38.4	0	0%
BTC-VC	2	21.6	22.7	0	0%

Table XVI: Acute Zinc Water Quality Exceedances

Site Name	n	Minimum (µg/L)	Minimum (µg/L)	Number of Exceedances	Percent of Exceedances
GG-01	7	36.9	396.0	2	29%
GG-02	0	--	--	0	0%
GG-03	5	56.8	1051.0	2	40%
GG-04	5	191.7	446.6	5	100%
GG-05	7	54.4	1999.0	5	71%
GG-06	3	9.1	230.5	1	33%
GG-07	5	937.3	3901.0	5	100%
GG-08	0	--	--	0	0%
GG-10	7	4.3	37.6	0	0%
BTC-US	2	14.8	38.4	0	0%
BTC-VC	2	21.6	22.7	0	0%

For baseflow conditions, 33% of samples taken exceeded chronic aquatic life standards for zinc (Table XVII). All of the sampling locations except the upstream concrete culvert (GG-10) and the weir (GG-02) had one or more exceedances for zinc for baseflow conditions. The wooden culvert (GG-07) contained the highest concentration of 3577 ppb zinc, which was over fourteen times the hardness adjusted standard. The downstream combined culvert (GG-05), 29% of the samples exceed zinc, with the max concentration being almost eight times the hardness adjusted value of 289.2 ppb.

Table XVII: Chronic Zinc Water Quality Exceedances

Site Name	n	Minimum (µg/L)	Minimum (µg/L)	Number of Exceedances	Percent of Exceedances
GG-01	5	45.7	354.9	1	20%
GG-02	2	63.3	238.7	0	0%
GG-03	4	32.1	507.9	3	75%
GG-04	5	36.8	1200.0	4	80%
GG-05	7	37.3	2294.0	2	29%
GG-06	6	10.4	50.7	0	0%
GG-07	7	134.7	3577.0	4	57%
GG-08	2	2.5	193.3	1	50%
GG-10	3	13.2	17.5	0	0%
BTC-US	0	--	--	0	0%
BTC-VC	0	--	--	0	0%

3.4.3. Heavy Metal Loading Rates

Heavy metal sampling and flow rate were conducted on Gove Gulch at the GG-01 location to determine loading rates into BTC. Table XVIII lists the flow conditions, flow rates, and loading rates for TRM for copper, iron, and zinc. Loading rates highlighted in red are sampled concentrations that also exceeded MTDEQ Circ-7 acute and chronic aquatic life standards.

Table XVIII: Heavy Metal Loading Rates at GG-01 (Note: Loading Rates Highlighted in Red Exceed Acute and Chronic Life Standards)

Date	Flow Condition	Flow Rate	Copper	Iron	Zinc
		cfs	(lb/day)	(lb/day)	(lb/day)
5/18/2018	Wet Weather Flow	1.94	0.77	9.20	4.13
6/5/2018	Normal High Flow	3.04	1.43	20.74	1.81
6/18/2018	Wet Weather Flow	10.37	0.63	104.53	10.34
7/9/2018	Wet Weather Flow	2.55	0.04	6.58	1.24
7/17/2018	Normal High Flow	1.15	0.00	2.91	0.32
8/16/2018	Normal High Flow	0.30	0.01	0.58	0.08
9/13/2018	Baseflow	0.50	0.02	0.50	0.10
9/27/2018	Baseflow	0.48	0.05	0.43	0.40

Water quality data that was attained by EPA Remediation Program Manager Nikia Greene was used to supplement data being acquired on Grove Gulch. Loading rates for BTC and Grove Gulch from the EPA were averaged and compared with loading rates from base flow sampling data at GG-01 (collected for this thesis) (Figure 29). The zinc loading rate contribution from Grove Gulch to BTC from 2009 EPA sampling data was 0.057 lb/day (average of five samples). The zinc loading rate contribution from sampling this summer was 0.43 lb/day (average of three samples). The average calculated downstream BTC loading rate from EPA samples was 0.63 lb/day (average of eighteen samples) (Figure 29) (Nikia Greene, EPA). Using a mass balance, the upstream loading rate on BTC before the contribution from Grove Gulch was calculated to be 0.34 lb/day.

Stormwater sampling data on Grove Gulch, provided by the EPA, used an ISCO water sampler which was used to sample at multiple times during storm events. Loading rates were then calculated using the provided flow rates, and TRM and TDM concentrations from the EPA. For copper, arsenic, lead, and zinc, calculated loading rates were compared to the flow hydrograph from a storm event on 6/5/17. All heavy metals showed an increase in loading rate throughout the peak hydrography of the storm event (Figure 30). The difference between TRM and TDM zinc loading rates were analyzed and showed that a large fraction of zinc was contained in the undissolved fraction (Figure 31).

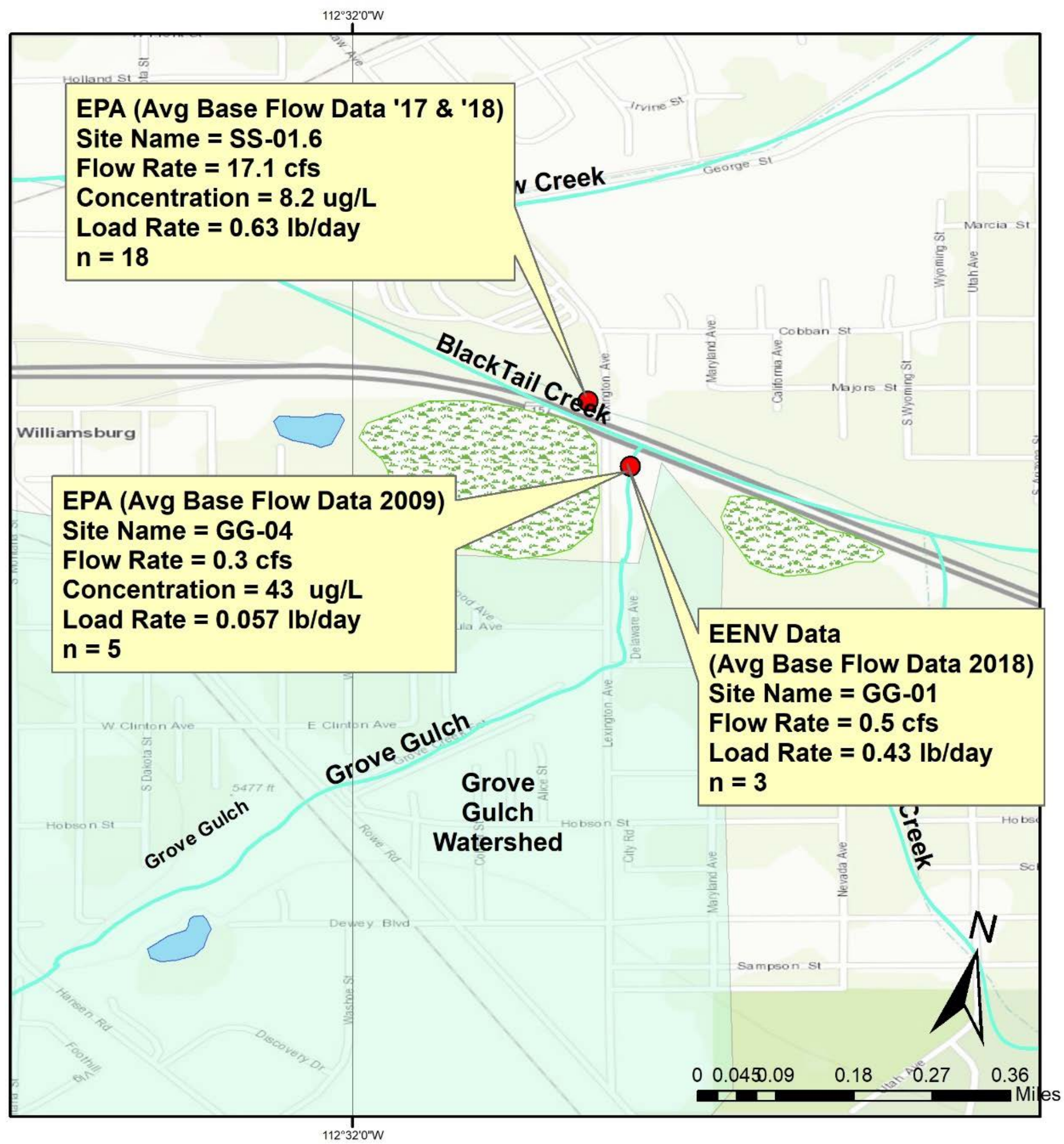

Figure 29: Average heavy metal loading rate for TRM for 2009, 2017 and 2018 (Nikia Greene, EPA)

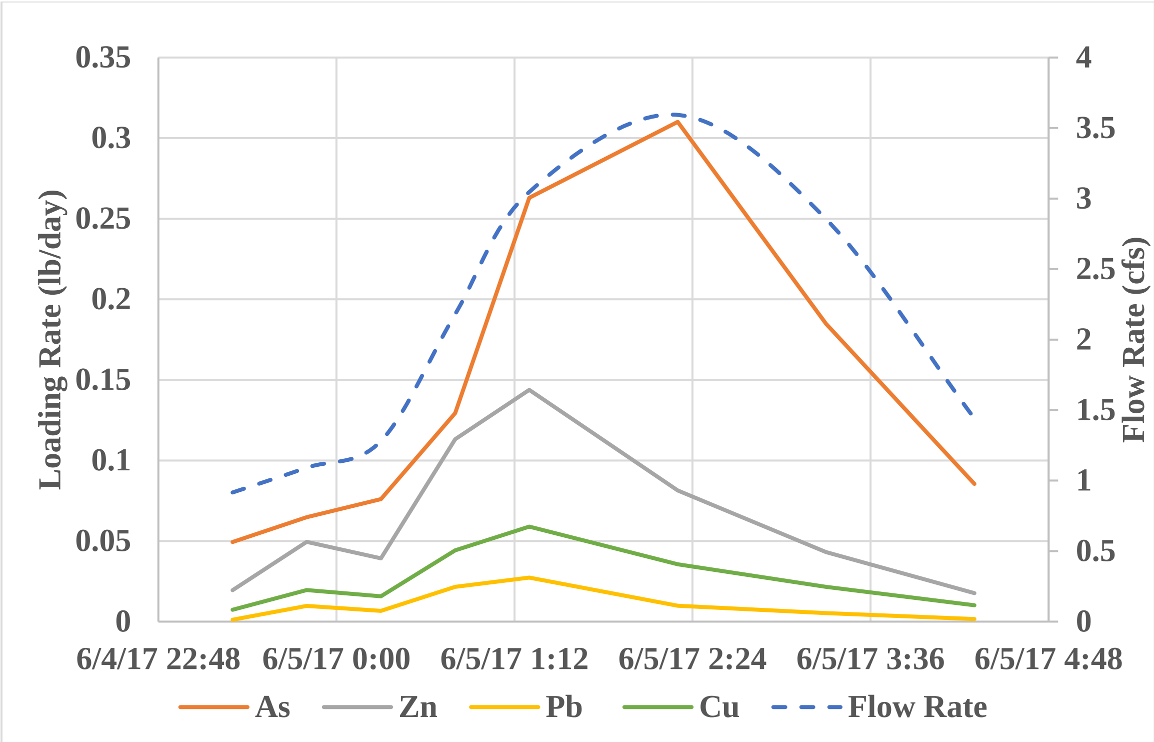

Figure 30: Heavy metal loading rate for TRMs on 6/5/17 (Nikia Greene, EPA)

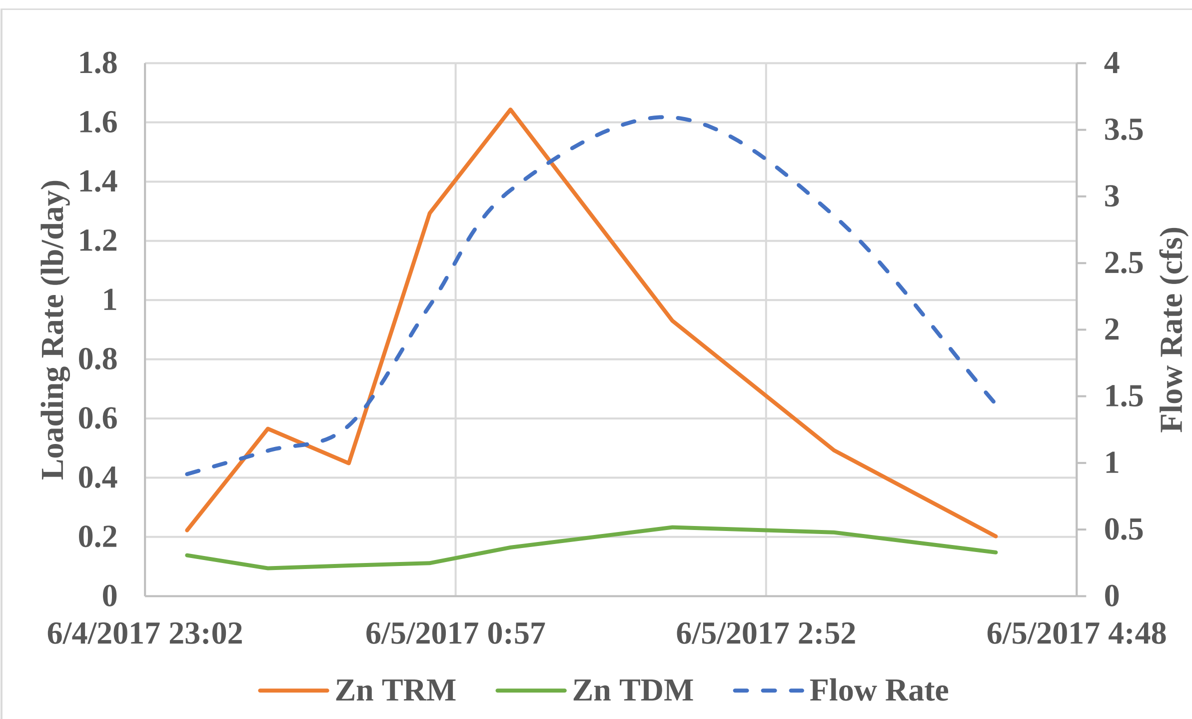

Figure 31: Difference between TRM and TDM loading rates for a storm event on 6/5/17 (Nikia Greene, EPA)

3.5. Heavy Metal Concentration in Soils

Soil sampling was conducted along Grove Gulch and the surrounding watershed. In total 53 soil samples were taken, with 27 samples being analyzed with an ICP-OES and the remaining screened with an XRF. Samples concentrations were also sent to MarCOM labs and the MBMG analytical laboratory to verify samples analyzed in-house. Figure 7 shows the geospatial locations of the different soil samples taken.

3.5.1. Arsenic

The recreational standard, set by the BPSOU ROD, for arsenic is 1000 ppm in the soil. Elevated levels of arsenic were found geospatially around the outside perimeter of the CMRC to the south and south-east. Soil samples near the Grove Gulch bank and inside the CMRC shows non-elevated levels of arsenic. The soil sampling results for Grove Gulch showed 2 of the 27 samples exceed recreational standards around the CMRC perimeter (Figure 32).

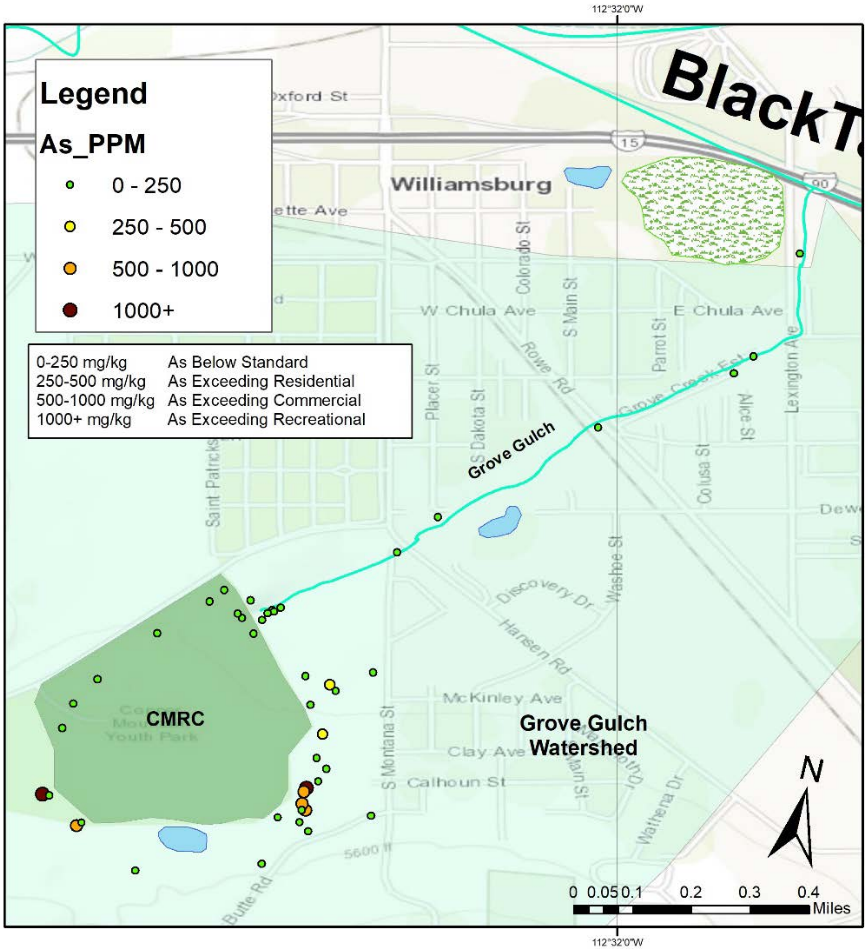

Figure 32: Arsenic soil concentrations and locations

3.5.2. Copper

The results of soil sampling for copper showed elevated concentrations around the boundary of the CMRC and along the banks of Grove Gulch (Figure 33). The BPSOU ROD does not specify a specific remedial action clean up level for copper in soil (US EPA, 2006). The elevated copper sampling results are shown in Figure 33.

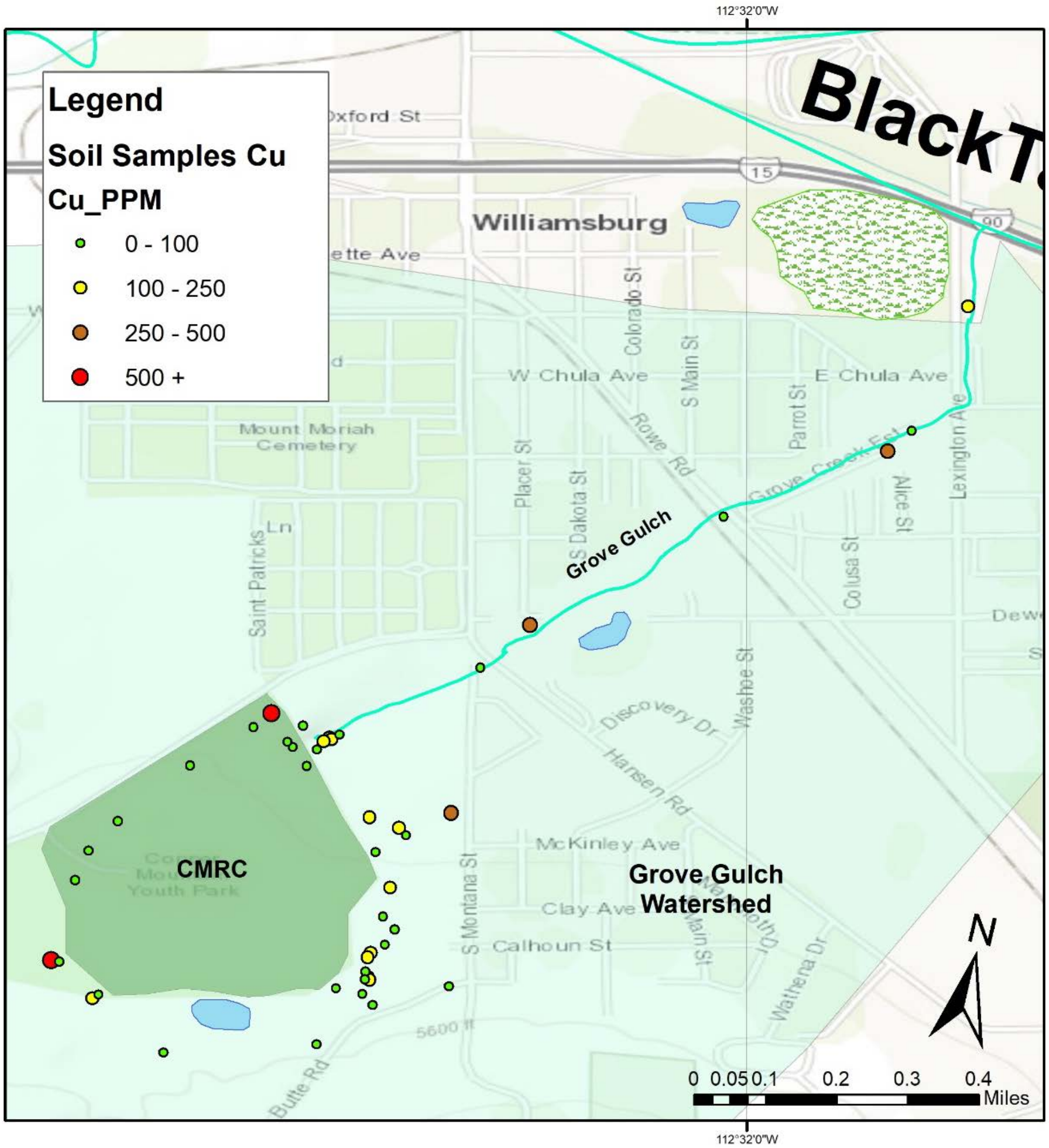

Figure 33: Copper soil concentrations and locations

3.5.3. Lead

Lead concentration was elevated near the CMRC and along the banks of Grove Gulch (Figure 34). There is no recreational standard for lead but there is a residential standard of 1200 ppm. Two samples exceeded residential standard levels but are located in recreational areas so technically do not exceed the standard. Samples inside the CMRC property showed elevated signs of lead concentrations but no samples exceeding recreational standards.

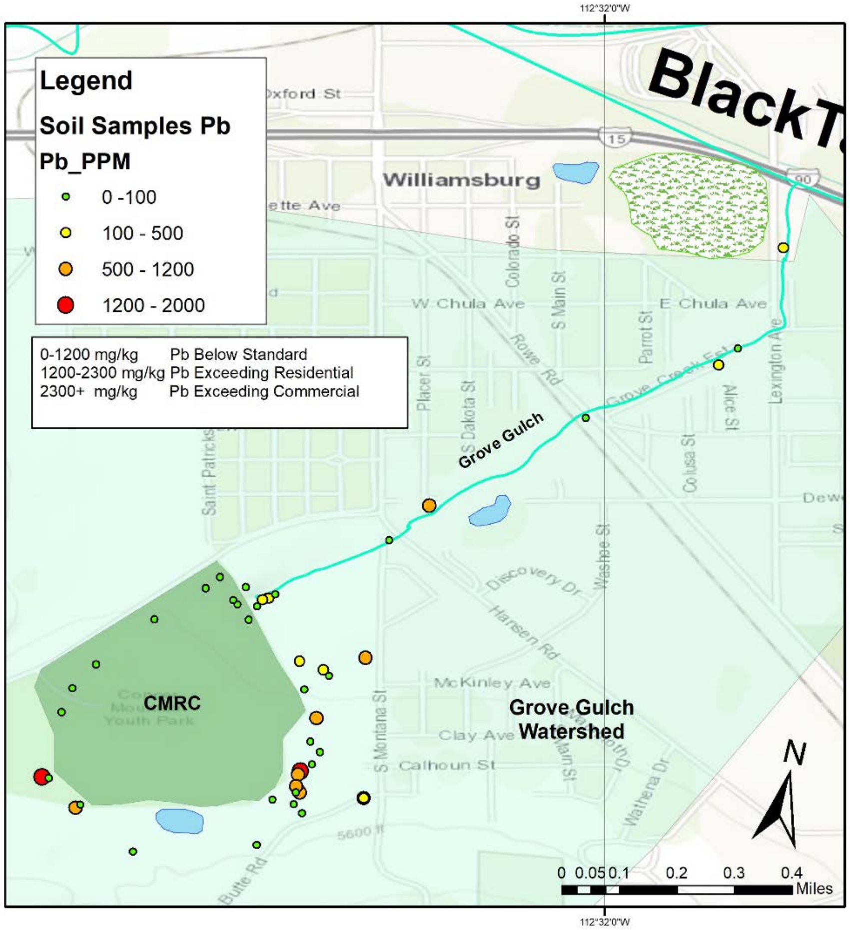

Figure 34: Lead soil concentrations and locations

3.5.4. Zinc

The results of soil sampling for zinc showed elevated concentrations around the boundary of the CMRC and along the banks of Grove Gulch (Figure 36). BPSOU ROD does not specify remedial action cleanup levels for zinc contamination in soils (US EPA, 2006). Areas between the historical location of the Timber Butte Zinc Mill and the CMRC show elevated levels of zinc concentrations (Figure 35).

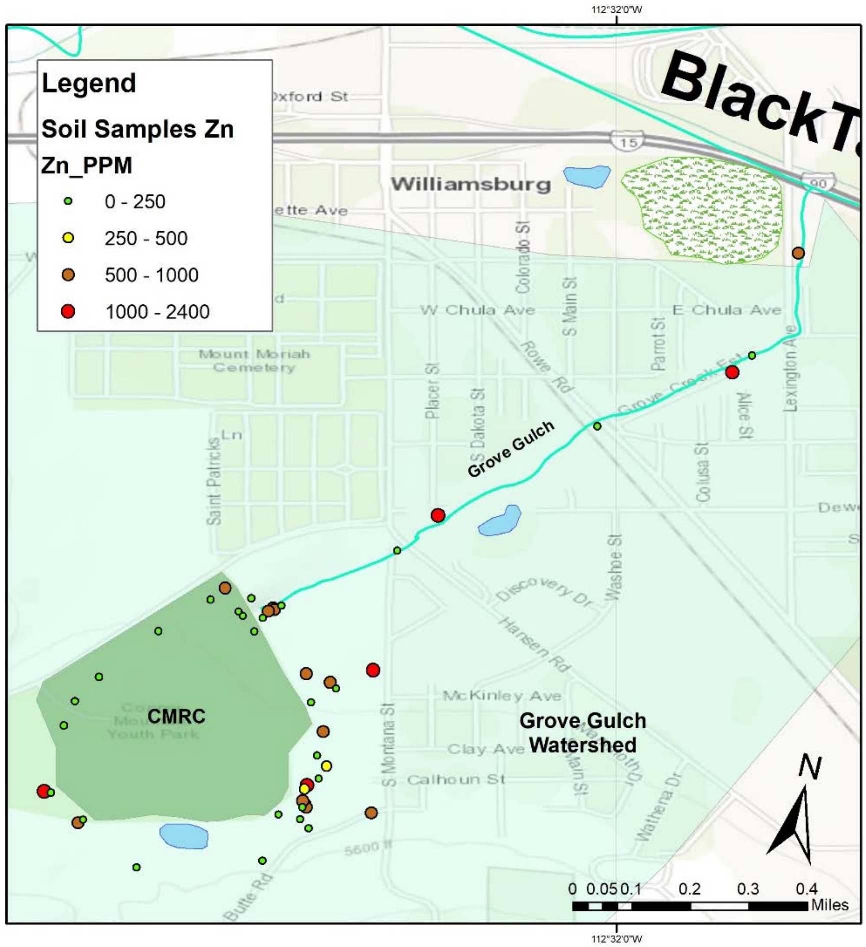

Figure 35: Zinc Soil Concentration and Locations

3.6. Heavy Metal Concentration in Sediments

Grove Gulch streambed sediments were sampled and analyzed for heavy metals deposited on the bottom of the creek. There are no heavy metal standards for sediment materials set by the BPSOU ROD, nor specific thresholds set by MTDEQ or the EPA. However, the National Oceanic Atmospheric Administration (NOAA) developed Sediment Quality Guidelines (SQG) used by scientists to further understand sediment chemical characteristics and their effects on aquatic environments. SQGs are neither promulgated by regulatory criteria nor to be considered standards. They are only intended as an informal guideline for interpreting sediment quality data (NOAA, 1999). The SQGs were derived from extensive studies from around the United States that were compiled and analyzed to develop the guidelines and are meant to be paired with toxicology analysis. The Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) are used in the SQG for screening to assess sediment quality. Table XIX lists the PEC and TEC values for the different heavy metals.

Table XIX: Sediment Quality Guidelines TEC and PEC Thresholds (DNR Wisconsin, 2003)

Metals	TEC (mg/kg dry wt.)	PEC (mg/kg dry wt.)
Arsenic	9.8	33
Copper	31.6	149
Lead	35.8	128
Zinc	121.0	459

Fifty-eight sediment samples were collected for Grove Gulch (Figure 8). Of those 58 samples, were pre-screened with an XRF and 27 samples were analyzed by an ICP-OES. For ICP-OES analysis, 16 samples were analyzed in-house in the Environmental Engineering department, 7 samples were analyzed by the MBMG analytical laboratory, and 12 samples were crossed verified by MarCOM labs.

3.6.1. Arsenic

Of the 24 samples analyzed for arsenic by an ICP-OES, 21% were elevated above the TEC threshold value for arsenic of 9.79 ppm (Figure 36). The remaining 79% of samples all exceeded the PEC threshold of 33 ppm for sediment. The wooden culvert (GG-07) showed the highest concentrations of arsenic (range 14 to 708 ppm) in sediments. The trailer park (GG-03) also had elevated levels of arsenic (range 13 to 115 ppm) above PEC thresholds in sediment samples.

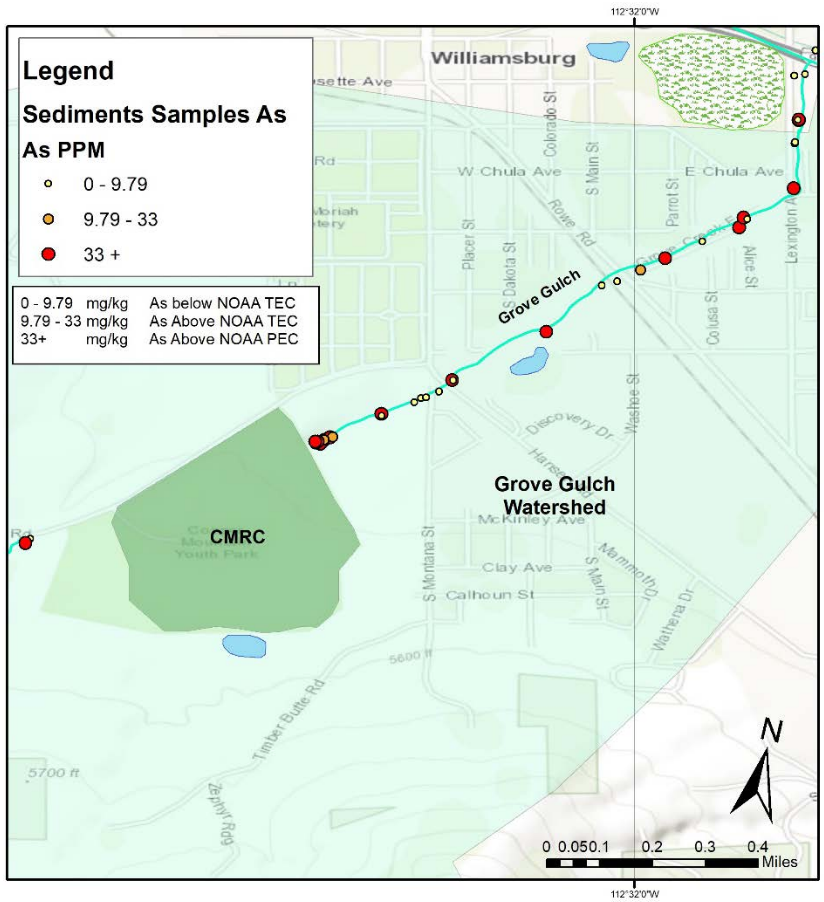

Figure 36: Arsenic concentrations in sediment samples along Grove Gulch

3.6.2. Copper

Out of the 24 samples analyzed for copper by the ICP-OES, 25% of the samples were elevated above TEC thresholds while 63% of the samples were elevated above PEC thresholds (Figure 37). The sediment samples located near the wooden culvert (GG-07) were elevated (ranged from 34 to 666 ppm) for copper with 7 of the 10 samples elevated above 100 ppm. Copper concentrations were also elevated (range from 72 to 500 ppm) for the trailer park (GG-03) samples (Figure 37).

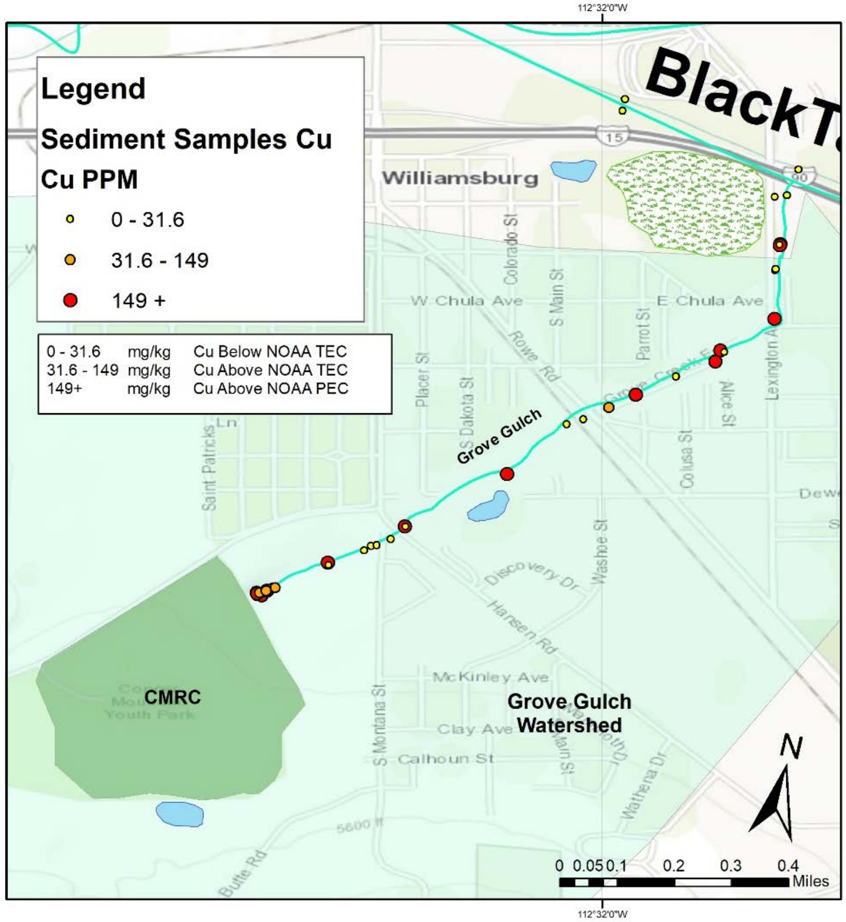

Figure 37: Copper concentrations in sediment samples along Grove Gulch

3.6.3. Lead

Out of the 24 samples analyzed for lead by the ICP-OES, 29% of the samples were elevated above TEC thresholds while 33% of the samples were elevated above PEC thresholds (Figure 38). Lead concentrations were also elevated (range from 64 to 370 ppm) near the trailer park (GG-03).

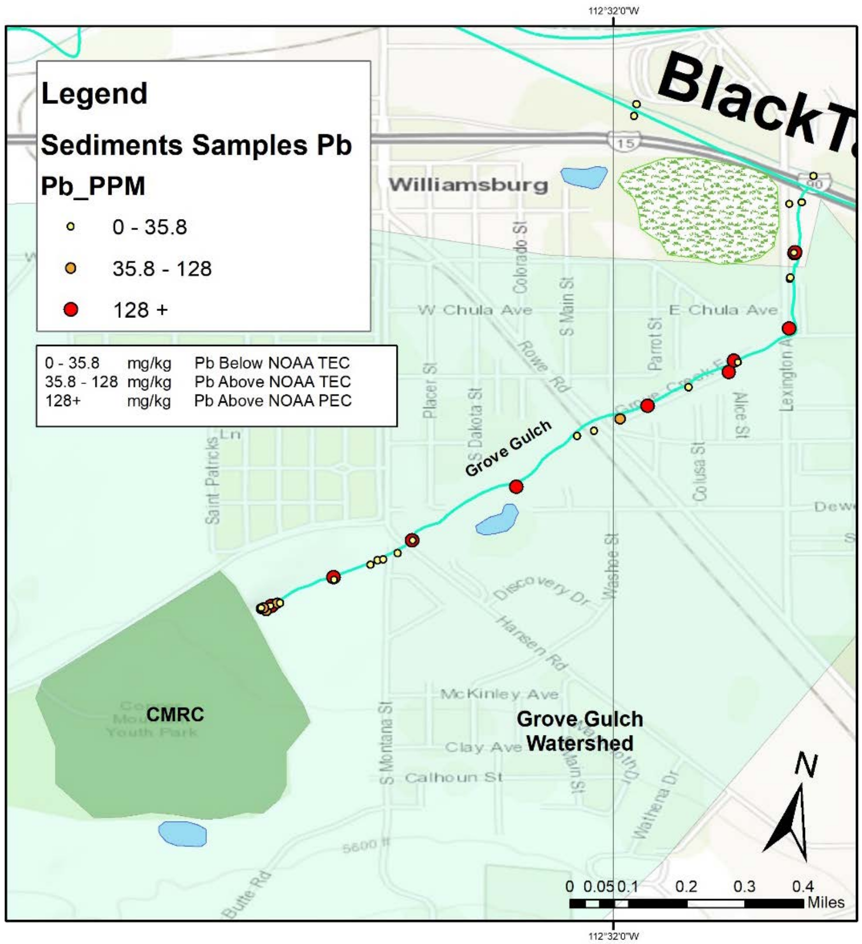

Figure 38: Lead Concentrations In Sediment Samples Along Grove Gulch

3.6.4. Zinc

Out of the 24 samples analyzed for zinc by an ICP-OES, 12% of the samples were elevated above TEC thresholds while 83% of the samples were elevated above PEC thresholds (Figure 39). Zinc concentrations were elevated (range from 270 – 5482 ppm) for the wooden culvert (GG-07). The trailer park (GG-03) had zinc sediment concentrations elevated (range from 300 to 1560 ppm) in the sediment samples.

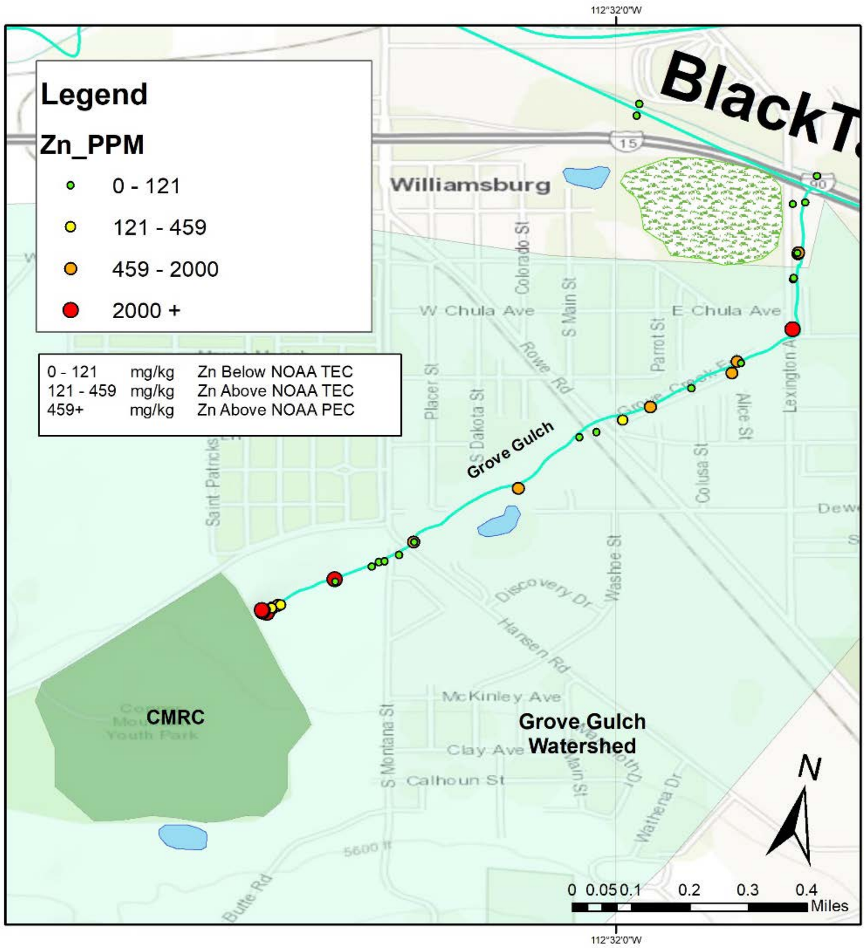

Figure 39: Zinc Concentrations In Sediment Samples Along Grove Gulch

3.7. Groundwater

Groundwater can contribute to surface water flow throughout the year if the surrounding groundwater table or potentiometric zone is above the river stage elevation. Groundwater is typically recharged from mountain snowmelt and surface water sources. From visual observations, it is possible to assume that Grove Gulch is affected by groundwater along different reaches throughout the length of the stream. In order to determine the sections of groundwater that contribute to Grove Gulch visual observations and analysis of collected historical well logs from MBMG GWIC were used to understand groundwater characteristics in the Grove Gulch watershed.

Using groundwater well data, a potentiometric contour map was developed using ArcGIS (Figure 40). One limitation of this data is that static water levels were not acquired at the same time because the well log data GWIC has accumulated can range from the 1980s to the present. Using water elevation data, a raster was developed to compare with the surface elevation data acquired from the USGS. The water elevation raster data was used with the surface elevation raster to produce a 3D representation of the potentiometric water level with the surface elevation. Using this 3D model, it was possible to determine visually the regions along Grove Gulch that are groundwater gaining and groundwater losing sections (Figure 41). Using the potentiometric water level, the groundwater gaining and losing reaches were approximated. The upper section of Grove Gulch is mostly gaining while the lower section below the CMRC transitions to groundwater losing. Lastly, the lower section of Grove Gulch that runs along Lexington Avenue changes back to groundwater gaining (Figure 42). The lower section of Grove Gulch was not classified as groundwater gaining, which could possibly be because of the lack of groundwater well data in that area. During baseflow conditions, some sections dry up and do not have any water flowing, while other sections stay flowing and support wetlands along the Grove Gulch.

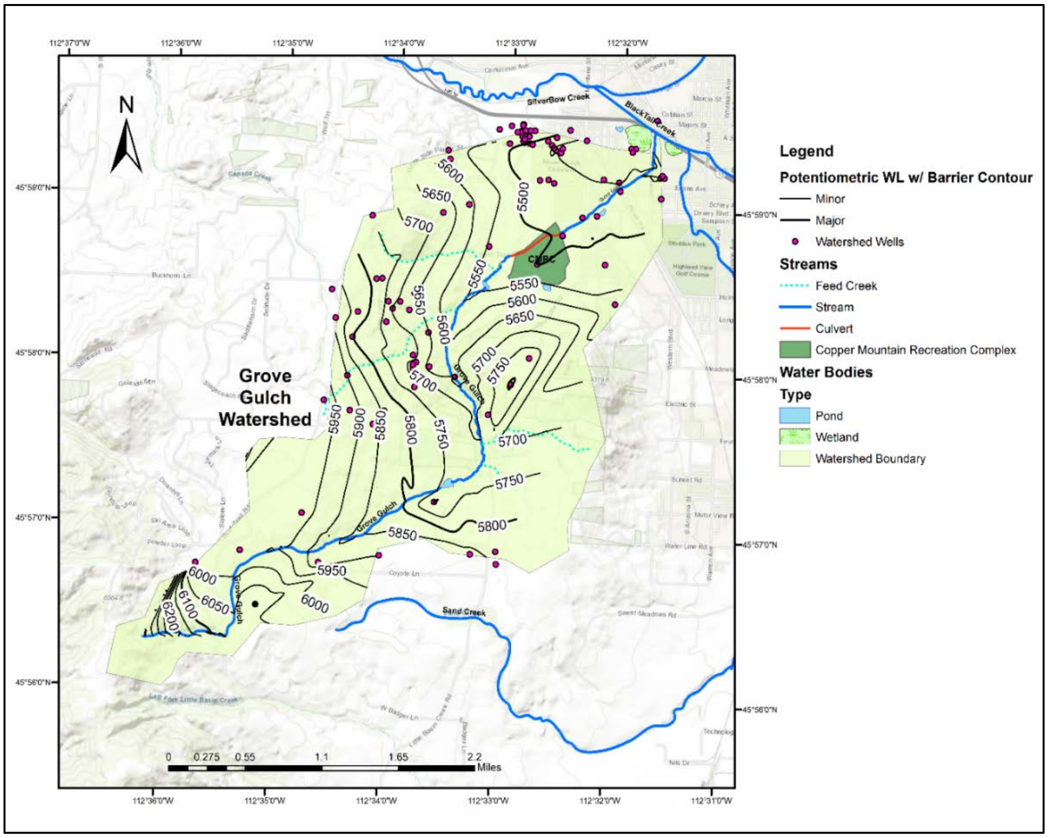

Figure 40: Groundwater potentiometric water levels

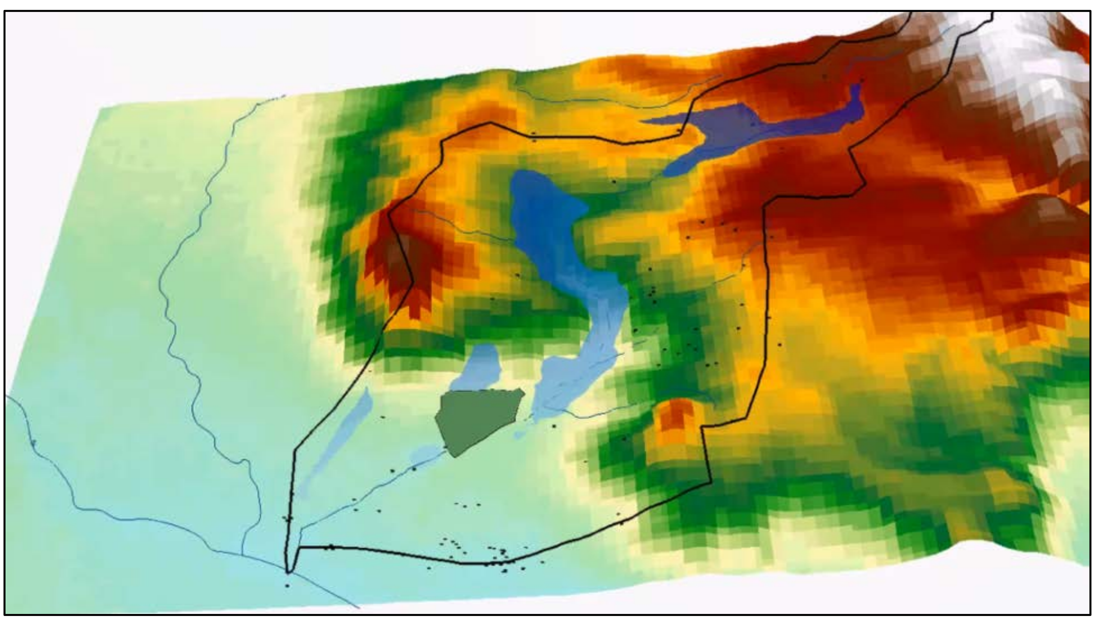

Figure 41: 3D map of potentiometric water level above surface elevation

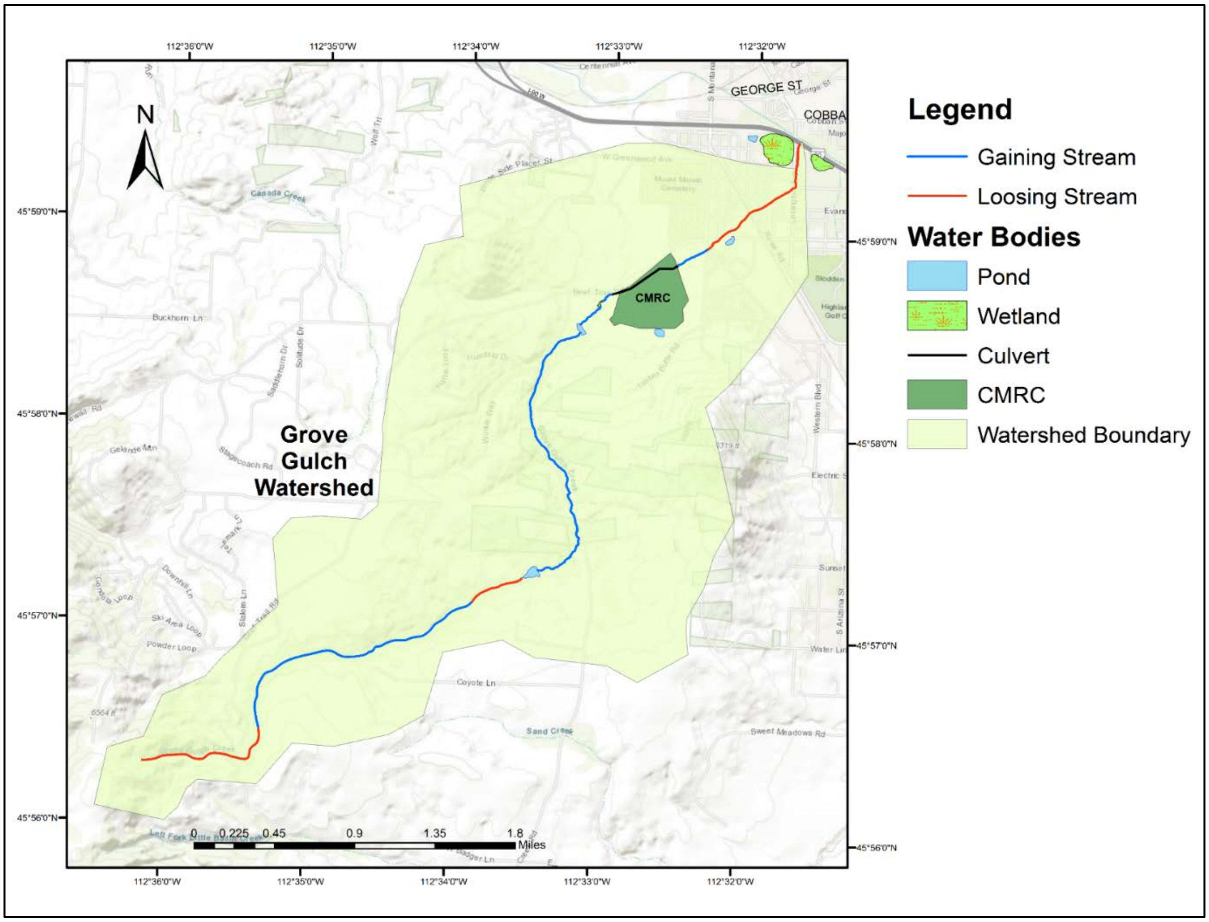

Figure 42: Gaining and losing sections of Grove Gulch)

3.8. Quality Assurance & Quality Control

During the course of acquiring data for this thesis, steps were put in place to track the quality assurance and quality control (QA/QC). If the field, DI blanks were transported with the sampling bottles, along with taking field duplicates. In the lab, lab-fortified duplicates were analyzed along with lab-fortified DI blanks. Samples were cross-analyzed and sent to the MBMG Analytical and MarCOM Laboratory. During analysis with the ICP-OES, continuous calibrations were analyzed to ensure high-quality data was acquired. Tables showing the QA/AC results for this thesis are contained in Appendix A.

4. Discussion

The data produced from this thesis work was used to characterize the Grove Gulch watershed and identify the sources of heavy metals. Field data and laboratory analysis were used to characterize surface water quality, watershed soil, and streambed sediment heavy metal concentrations for Grove Gulch. Heavy metals are often released from the results of mining operations such as mining, milling, concentrating, and smelting. Grove Gulch is the location of the historic Timber Butte Zinc Mill and has exhibited similar characteristics associated with environmental contamination from mining activities.

The results from this thesis were used to help identify heavy metal sources affecting known water quality issues along Grove Gulch. Soil sampling was conducted to characterize exposed mine tailings between the Zinc Mill and the CMRC that could expose heavy metals to recreational users. <u>The major source of heavy metals in Grove Gulch originates from the in-place Clark along the path of Grove Gulch.</u> These tailings have since been impounded and buried but sources of heavy metals are still prevalent in and around the CMRC and are being released by groundwater flow from the old wooden culvert.

4.1. Sources of Heavy Metals

4.1.1. Exposed Clark Tailings

The Clark Tailings, characterized in section 1.2.1, contained known sources of heavy metals specifically zinc and iron, with traces of arsenic, cadmium, copper, and lead. The Clark Tailings where buried to prevent continued release of eroded material and to reduce the exposure to human health on the surface. Based off of visual and analytical observations it is obvious that there are still tailings material between the old Zinc Mill and around the perimeter of the CMRC. These exposed tailings when exposed to weathering, can be mobilized and transported towards

Grove Gulch which observed by sampling overland flow, during a precipitation event, from the direction of the Zinc Mill drainage towards Grove Gulch. This sample contained elevated levels of copper which would exceed water quality standards once discharged into Grove Gulch. The drainage below the Zinc Mill has visible signs of tailings material, coloring of the soil, and minimal vegetation growth (Figure 43).

Figure 43: Exposed tailings material around the perimeter of the CMRC

4.1.2. Buried Clark Tailing

A majority of the Clark Tailings that were impounded along the path of Grove Gulch were buried and capped with the creation of the CMRC. These buried tailings originally used a wooden culvert to transport Grove Gulch surface water flow underneath the tailings. In 1982 the wooden culvert was replaced with a larger concrete culvert. The buried tailings could be mobilizing and transporting heavy metals via groundwater into the Grove Gulch watershed.

4.1.2.1. Wooden Culvert Underneath the CMRC

Originally, the thought was that the wooden culvert had been removed but currently it is still discharging into Grove Gulch. This point source is acting like a groundwater sump and draining heavy metal-laden groundwater out of the Clark Tailings and surrounding aquifer into Grove Gulch. Extensive sampling of this point source discharge concluded that elevated levels of heavy metals were being discharged into Grove Gulch and mixing with relatively non-elevated concentrations of heavy metals from upstream Grove Gulch. This addition of heavy metals loading caused exceedances for human health standards and aquatic life standards in Grove Gulch downstream of the CMRC.

4.2. Feasibility Study

Heavy metal loading from Grove Gulch being discharged into BTC previously studied known issue (Craig, 2016) and one method of minimizing these effects are implementing Best Management Practices (BMPs). For the purpose of this thesis, four major remediation criteria were considered to compare the difference remedial options against each other. The four criteria considered were technical feasibility, cost-benefit analysis, environmental benefits, and lastly human health as safety. A decision matrix was developed by weighing the different remediation criteria, researching the different remedial options, and then assigning weighted values based on the available resources and benefits to the environment and human health.

Different weighted values for each criterion were assigned and used in a decision matrix. This decision matrix was then used to pick the best remedial option(s) for Grove Gulch. The decision matrix comparing the different remediation options is detailed in Table XX. Individual remediation options will be further discussed in the following sections. The weighted values were picked by analyzing the different criteria specified in the Upper Clark Fork River Basin restoration grant review guidelines, and higher weighed criteria were decided based on human health safety and overall feasibility (BNRC, 2009). The overall rating for the different remediation options was based on available resources and proven technology and how effectively it would reduce heavy metals.

Table XX: Remedial Option Decision Matrix

Option	Technical Feasibility	Cost vs Benefit	Environmental Benefits	Human Health and Safety	Score
Retention Basins	95	90	85	70	**85**
Sulfate-Reducing Bio-Reactor	75	95	90	90	**90**
Soil Remediation	90	80	80	80	**83**
Removal of Wooden Culvert	50	50	70	80	**63**
Stream Channel Lining	70	50	70	60	**62**
Do Nothing Option	100	30	30	30	**49**

(weight values = Technical Feasibility 27%, Cost vs Benefits 23%, Environmental Impact 20%, Human Health and Safety 30%)

4.2.1. Retention Basins

Retention basins are well-studied engineering solution used to reduce peak flows, capture sediment, and reduce pollutants like sediments, nutrients, and heavy metals in surface water runoff. There are also many different types of retention basins, each with their own benefits. These different types of retention basins are listed in Table XXI along with a brief description.

Table XXI: Types of Retention Basins (USEPA, n.d.)

Type of Basin	Description
Detention Basin	Captures runoff and temporarily retains the volume captured
Retention Basin	Captures and maintains a volume of runoff until another runoff event occurs displacing original runoff
Constructed Wetland Systems	Similar to a retention or detention basin only contains wetland vegetation
Filtration Basin	Captures runoff and uses granular filtration media such as sand or membrane to remove constituents

There are many different types of mechanisms that affect how pollutants are removed from retention and detention basins. These mechanisms are sedimentation, filtration, infiltration, and biological conversion. Sedimentation, which is the removal of suspended particulates by gravitational settling, can also reduce pollutants that are attached to the particulates, like heavy metals for example. Filtration is the removal of particulates by passing water through a porous media. Infiltration can filter out sediments, metals and dissolved constituents into the ground by a process of filtration and adsorption. The technical feasibility was rated high because retention basins are widely used around the United States and currently 10 basins are already implemented in the BPSOU. One possible limitation to a retention basin on Grove Gulch is the high fraction of heavy metals contained in the dissolved component, which was observed from sampling. The cost-benefit analysis for retention basins was rated high because the general function and design of a retention basin are fairly simplistic. The cost for retention basins can increase with the addition of extra components like adding filtration beds or vegetation but can also increase the reduction of contaminants. The environmental benefit rating was an 85 because the basin will control runoff and sediments well but might struggle to capture the dissolved fraction of heavy metals present. Lastly, the human health and safety rating was a 70 because the retention basin is only preventing elevated levels of heavy metals from entering BTC, and not keeping elevated levels of heavy metals away from the public along Grove Gulch. Overall, a retention basin would be effective at reducing the heavy metal loading to BTC during runoff by reducing heavy metals by 50% to 80% and sediments by 70% (USEPA, n.d.).

4.2.2. Sulfate-Reducing Bio-Reactor

Sulfate-Reducing Bio-Reactors (SRBR) are an in-situ remediation technique that utilizes bacteria to reduce sulfates naturally present in heavy metal contaminated waters. Sulfates are reduced into sulfide which is used to precipitate out metal hydroxides. Currently, laboratory experiments and small-scale field SRBR studied have proven effective at reducing heavy metal loads from the effluent. Removal efficiencies upward of 99% have been observed for copper, iron, and zinc (Craig, 2016). The technical feasibility was rated at 85 for SBR because the technology is well developed and feasibly but current implementations of the technology in the real world is limited. The cost-benefit analysis was rated fairly high at 90 because the design is fairly simplistic along with implementation and low operating and maintenance costs. The environmental benefit was fairly high, at 90, because there is a possibility to reduce upwards of 99% of heavy metals from the contaminated effluent. Human health and safety was rated at 90 because the reduction of heavy metals from a known source would reduce the exposure possibilities in Grove Gulch. Overall, a SRBR would be highly effective at reducing heavy metal concentrations along Grove Gulch with minimal long-term costs after implementation. Appendix B provides a draft estimate of volume and cost of the SRBR to treat the wooden culver discharge. An estimated size requirement and cost estimation for implementing a SRBR to treat the wooden culvert discharge is summarized in Appendix B.

4.2.3. Soil Remediation

Soil remediation along the perimeter of the CMRC would require further investigation to fully locate tailing materials not remediated with the CMRC. Soil remediation would then require surface regrading and the addition of a clean soil cap and revegetation. The technical feasibility of soil remediation is well known and shown to provide proven protection and reducing exposure and stabilizing in place tailings. The cost-benefit analysis was rated at 80 because of the benefits of minimizing exposure to the public and reducing the possibility of mobilization to Grove Gulch. Stabilizing the area around the CMRC would reduce runoff to Grove Gulch while also reducing exposure to human health which is why environmental benefit and human health and safety were rated at 80. Overall, soil remediation is effective remediation technique for stabilizing and reducing the mobilization of heavy metal contaminated media. The soil remediation option could also benefit the public by creating green space in the form of hiking trails or mountain bike trails around the outside often CMRC which is currently used by ATVs and dirt bikes.

4.2.4. Removal of Wooden Culvert

The wooden culvert is a proven source of heavy metal contamination that is discharging into Grove Gulch. The overall environmental benefits and human health and safety ratings for this remedial option were high because of the direct reduction of heavy metal loading into Grove Gulch from the wooden culvert would immediately remove the point source of heavy metals. On the other hand, the technical feasibility and cost-benefit analysis both rated at 50 because of the high level of unknown associated with the wooden culvert. In the process of removing the culvert the current remediation cap of the CMRC would be compromised during the excavation. Removing the wooden culvert might prevent surface discharge of groundwater directly into

Grove Gulch but might not reduce the flux of groundwater from flowing into Grove Gulch after removal of the culvert. Groundwater is known to impact Grove Gulch but the full understanding of the flow contribution into the creek and overall water quality would need further studying. The culvert also supplies a large volume of surface water flow to the creek (roughly half during baseflow conditions).

4.2.5. Stream Channel Lining

The concept of channel lining is not new to Butte and the surrounding area. Located on the Butte hill, concrete-lined channels are used on Missoula Gulch to divert runoff and overland flow to retention basins to remove sediments and other pollutants. The purpose of lining Grove Gulch would be to reduce the heavy metal loading from groundwater sources. Groundwater is a major source of surface water flow during baseflow conditions and has been observed as a major source of water contribution in the lower sections of Grove Gulch. The technical feasibility of lining the stream channel is pretty straightforward but could be difficult diverting the Grove Gulch flow to line the channel with concrete. The cost-benefit analysis was rated at 50 because of the overall unknown of the contribution of heavy metals from groundwater. Overall, without a full understanding of the groundwater impact along lower Grove Gulch, there is increased uncertainty of the environmental benefits of lining the Grove Gulch channel.

4.2.6. Do Nothing Option

The do nothing option for Grove Gulch is overall rated the lowest out of all the options. Doing nothing was scored the lowest in the decision matrix because human health and the environment benefit to Grove Gulch would not be impacted. The main purpose for the feasibility study for Grove Gulch is to reduce the human health exposure and heavy metal loading to BTC.

4.3. Potential Benefits to Grove Gulch and Blacktail Creek

The best remedial options for Grove Gulch based off of the results from this thesis are a combination of placing a retention basin at the base of Grove Gulch along, treating discharge from the wooden culvert with a SRBR, and remediating tailings material near the old Zinc Mill and around the CMRC. The reason why the combination of these three methods were selected, is because the retention basin would treat runoff water discharging from Grove Gulch into BTC, the SRBR would reduce heavy metals entering Grove Gulch from the Clark Tailings via the wooden culvert, and soil remediation would reduce the exposure and mobilization of heavy metals around the perimeter of the CMRC. The SRBR would reduce heavy metal concentrations while also reducing the human health hazard from elevated heavy metals in Gove Gulch. The retention basin at the base of Grove Gulch would capture, regulate flow, and treat contaminated particulates from normal high and wet weather flow conditions. The reduction of dissolved constituents of heavy metals from retention basins is highly dependent on the type of basin built. Table XXII summarizes the potential treatment benefits of using a SRBR to treat the effluent from the wooden culvert (GG-07) prior to discharge into Grove Gulch.

Table XXII: Heavy Metal Effluent Treatment Potential For The Wooden Culver (GG-07)

Heavy Metal	Pre-Treatment		Post-Treatment	
	Baseflow	Runoff	Baseflow	Runoff
Arsenic	32	29	0.316	0.294
Copper	37	144	0.371	1.439
Iron	8450	7820	84.5	78.2
Zinc	3577	3901	35.77	39.01

(Concentrations on are in ug/L)

5. Conclusions

The objective for this thesis was to characterize Grove Gulch in order to best recommend remedial options and BMPs to manage heavy metals. First, land use data, flow data, water quality data, and groundwater data were compiled to understand the characterization of Grove Gulch. Second, heavy metal concentrations and loading rates were investigated and calculated then sources were located. Finally, remedial options were investigated and a combination of three were recommended to improve Grove Gulch water quality and reduce human health hazards.

5.1. Grove Gulch Characterization

Grove Gulch is an intermittent stream which is heavily influenced by snowpack, precipitation and groundwater contributions. The watershed that feeds Grove Gulch is about 7 square miles in area with roughly 20.9% of the watershed being impacted or developed by human activity. Grove Gulch's water quality parameters (pH, ORP, DO) are of relatively good water quality, with DO concentrations dropping below 4 mg/L DO during warm baseflow conditions in late August. Grove Gulch has relatively low turbidity readings during normal flow conditions with ranges above 100 FNU during wet weather events. Turbidity measurements in the downstream sonde location (GG-02) showed elevated turbidity values when flow dropped below 1 cfs.

Groundwater is a known source to surface water contributions in Grove Gulch. In late July – September, the reach between Rowe Rd and Lexington Ave (GG-03) had no surface water flow, while just downstream, starting along Lexington Ave, Grove Gulch had surface water flow. Grove Gulch is somewhat interconnected to groundwater along the last reach of Grove Gulch along Lexington Ave, providing minimal flow to BTC. Although visual observations were made, overall quantifications on the extent of groundwater contributions are relatively unknown. Groundwater gaining and losing reaches were predicted using the MBMG GWIC database of groundwater wells. A majority of upper Grove Gulch is interconnected with groundwater, with the lower section more sporadically connected to groundwater sources.

5.2. Heavy Metal Loading and Sources

The results of sampling and analysis of surface water samples, soils and sediments along Grove Gulch showed elevated levels of heavy metals near the CMRC and flowing downstream to BTC. Heavy metal concentrations showed spatial variations with minimal heavy metals present upstream of the CMRC, highest concentrations being discharged from the wooden culvert (GG-02), and downstream concentrations decreasing till the last sampling location of GG-01. Variations in heavy metal concentrations were also observed during storm events with concentrations and loading rates both reaching peaks with flow increases from major wet weather events. Data analyzed from water sampling showed that Grove Gulch is heavily influenced by heavy metals with 50% of all samples (including upstream samples) exceeding MTDEQ Circular-7 hardness adjusted aquatic life standards. Arsenic and iron were measured in high concentrations, after being discharged from the wooden culvert (GG-07), causing successive samples downstream to exceed water quality human health standards and aquatic life standards. The most obvious source of heavy metal discharge into Grove Gulch is the wooden culvert causing elevated levels of heavy metals in downstream sampling.

Other heavy metals sources in the Grove Gulch watershed are exposed tailings around the CMRC and sediments deposited along the Grove Gulch streambed. These sources have the potential to be mobilized and impact the water quality of Grove Gulch. One such example was a wet weather sampling event on 4/29/18 where overland flow from the direction of elevated levels of heavy metals towards Grove Gulch showed levels of copper at 54.9 ppb. The concentration of copper was 8 times the hardness adjusted standard of 6.84 ppb if it was located in Grove Gulch. Soil sampling results showed 2 sampling sites exceeding BPSOU ROD recreational standards for Arsenic. Sampling for copper, lead, and zinc showed elevated levels around the perimeter of the CMRC. Sediment sampling showed most samples for arsenic, copper, lead, and zinc exceeding threshold effect concentrations or probable effect concentrations as defined by the SQGs by NOAA. Although these guidelines are meant for a screening purpose for analyzing sediment quality, the results should be paired with toxicology studies (which was not conducted as part of this thesis work).

5.3. Remediation Options

The purpose of conducting a remedial investigation and feasibility study on an impacted site is to develop remediation options and BMPs to reduce exposure to human health. The other reason for remediation options and BMPs is to reduce the mobility of contaminants. For this thesis, three remedial options were recommended to best reduce exposure, risk, and mobilization of heavy metals. The first remedial option would be a retention basin at the base Grove Gulch before discharging into BTC. A retention basin would regulate runoff and wet weather events, while also allowing sediments (with heavy metals attached) to settle out in the basin. There are many different types of retention basins that aid in capturing other contaminants (like dissolved heavy metals) by using filter beds, engineered wetlands, and infiltration but come at an increased cost.

The second remedial option would be to stabilize, cap with soil, and revegetate the exposed tailings material and soils around the CMRC. Currently, the area is used for walking dogs, dirt biking and ATVs, and hiking. The use of this area as a trail system for motorized vehicles increases the erosion of these tailings materials. One way to minimize this would be to create hiking trails or mountain bike trails to keep people on the trails and minimize damage to the remediation work. This would also increase the usability of the CMRC and increase the benefits to the surrounding community by developing the exposed area for recreational use.

The final proposed remedial option would be to control or remove the source of heavy metals being discharged into Grove Gulch by the wooden culvert. This culvert was extensively sampled over the course of a year and showed elevated levels of arsenic, iron, and zinc. The maximum concentration from the wooden culvert (GG-02) for arsenic was 31.6 ppb (3 times the human health standard). The maximum concentration for iron was 8.45 ppm (8.4 times the chronic aquatic life standard). Lastly, the maximum concentration for zinc was 3901 ppb (13 times the acute aquatic life standard). The remedial option that could treat the effluent from the wooden culvert would be through the use of a sulfate-reducing bio-reactor to treat the heavy metals. SRBRs have removal efficiencies for heavy metals >99% under the correct conditions.

6. Future Work and Recommendations

Based on the findings from this thesis, some future work is still required to fully characterize the Grove Gulch watershed to develop some remedial options.

6.1. Characterization of Groundwater

For this study, a historical groundwater investigation was completed using information available online. This data had limitations on how it could be used and on the accuracy of the data obtained because the well log data spanned between the 1980s to the present. In order to better understand the impact of groundwater on the lower section of Grove Gulch a radon study could be developed to see which reaches of Grove Gulch are affected by groundwater. Groundwater sampling should be conducted in existing wells if available. Another option would be to insert shallow aquifer wells along the creek to sample both groundwaters for heavy metals and measure water levels along the creek. Better understanding the contribution of groundwater to surface flow and heavy metal loading could help better develop remedial options for Grove Gulch

6.2. Field Testing for Subsurface Bio-Reactor

For this study, a SRBR was recommended as a remedial option to treat the heavy metal effluent from the Clark Tailings being discharged out of the wooden culvert. In order to accurately design the SRBR, laboratory experiments and field tests should be conducted with actual effluent water from the wooden culvert. This would provide a better understanding of possible removal rates for heavy metals.

7. References Cited

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8. Appendix A: Additional Results

8.1. TSS Loading Rate and Load Data

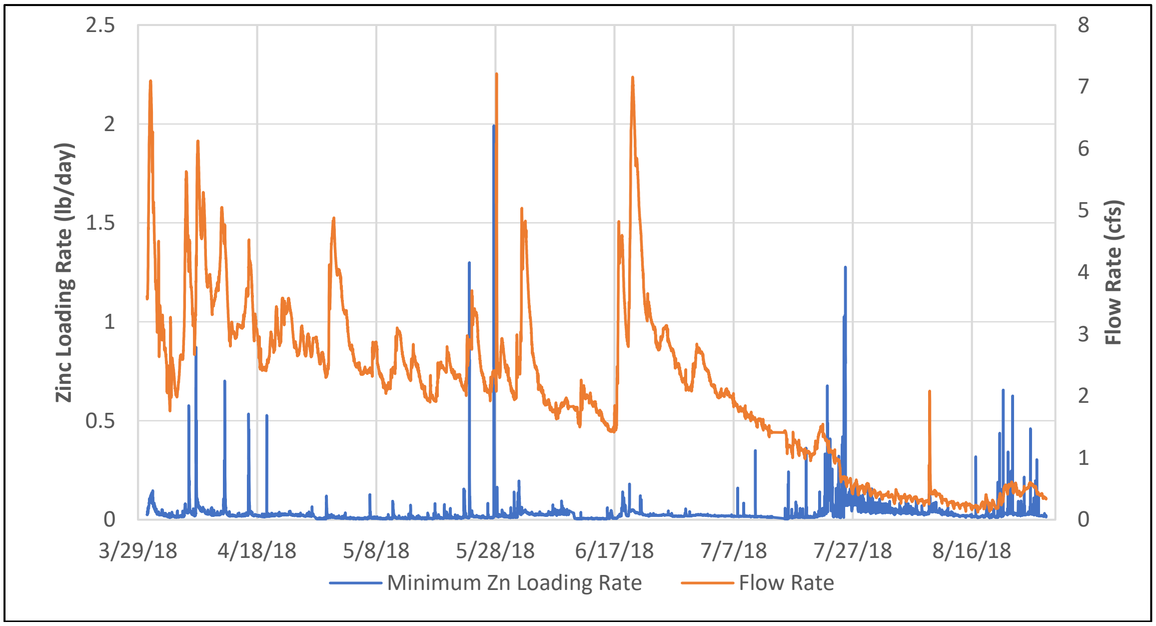


Figure 44: Flow rate vs calculated minimum zinc loading rates for GG-02

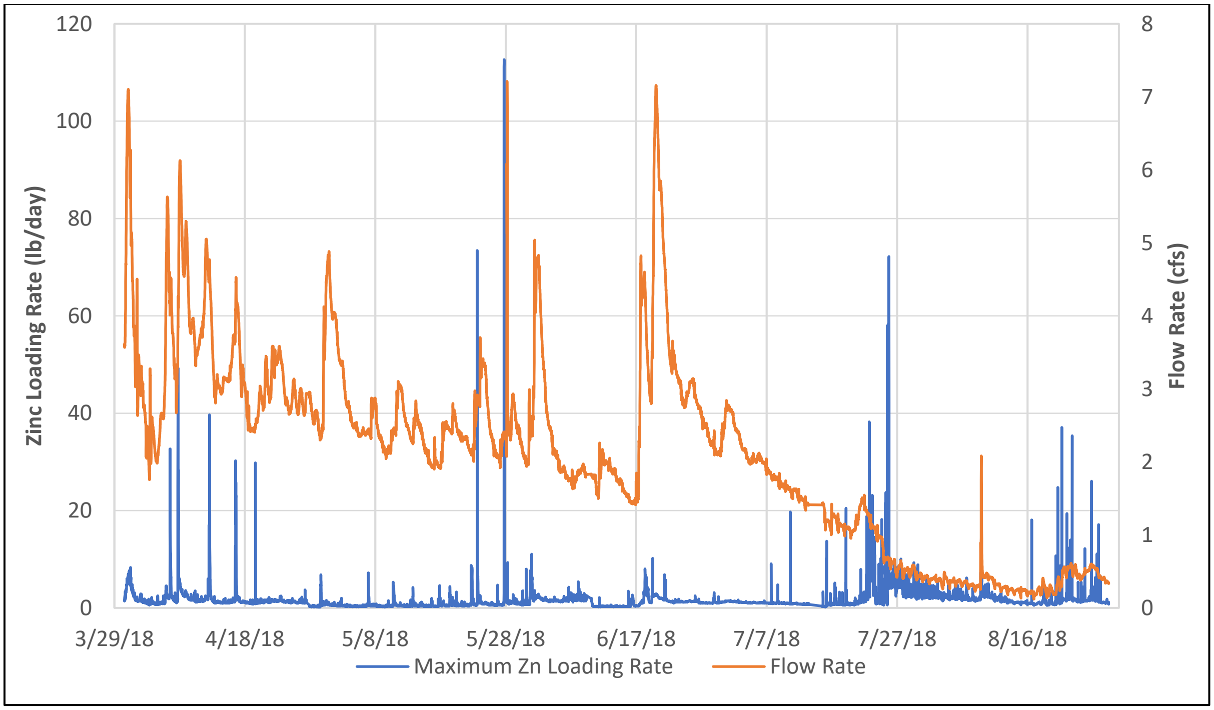


Figure 45: Flow rate vs calculated maximum zinc loading rates for GG-02

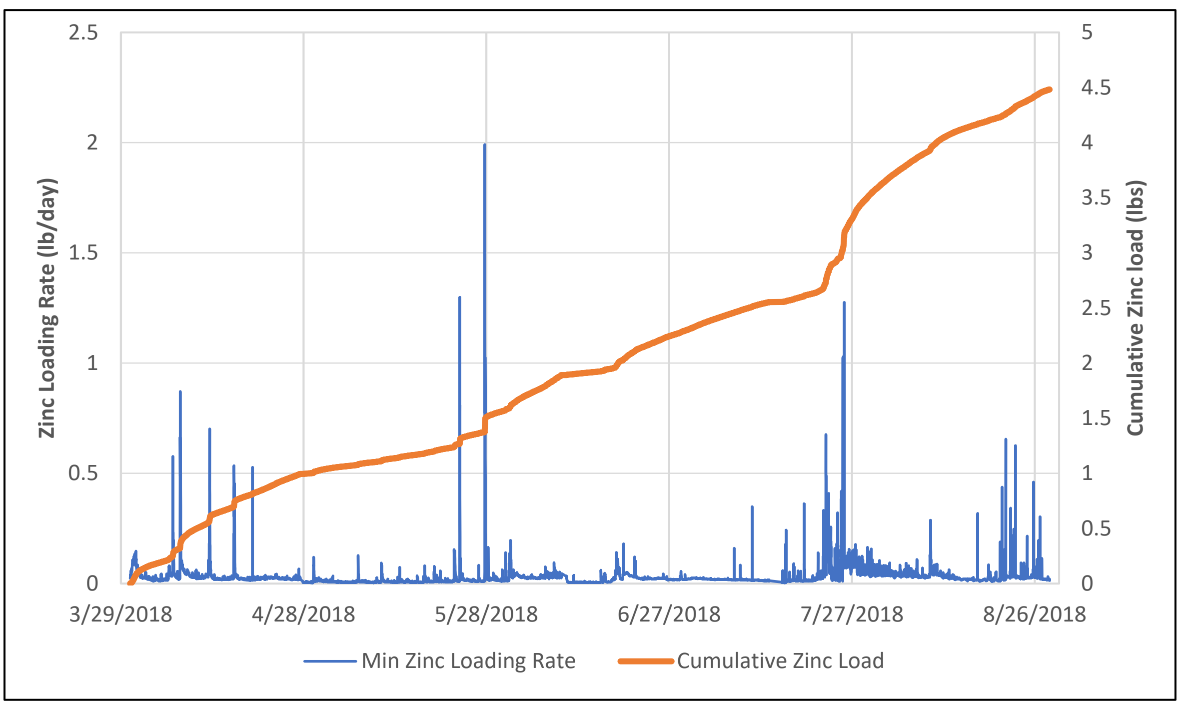


Figure 46: Calculated minimum zinc loading rates and cumulative zinc load

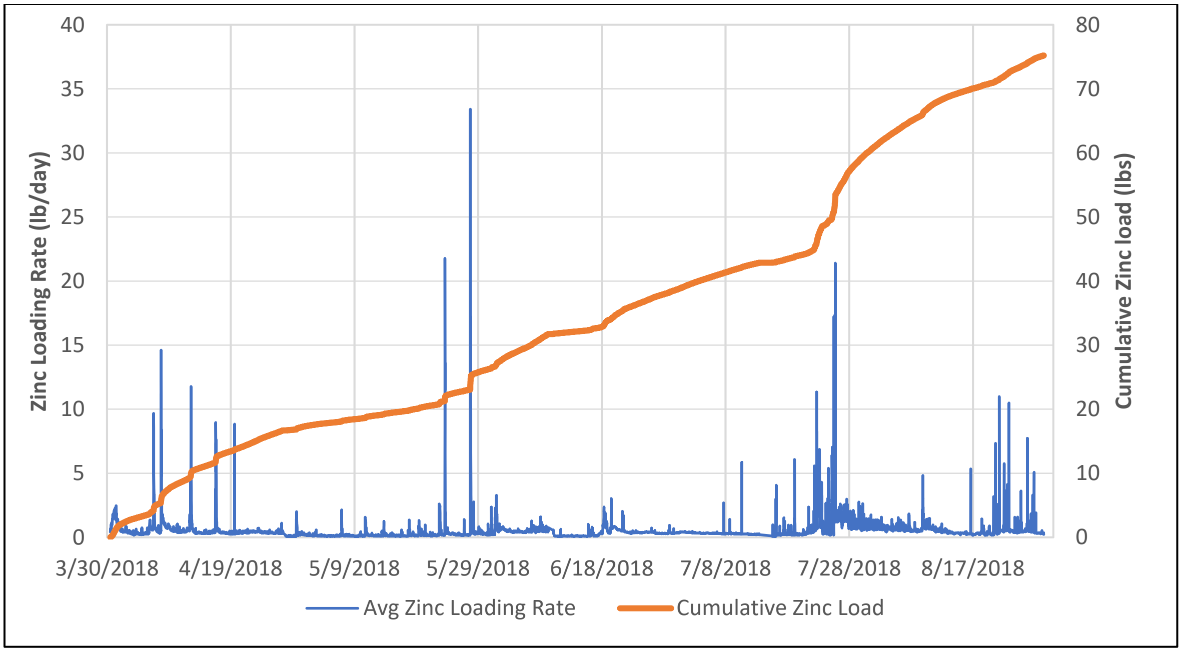


Figure 47: Calculated average zinc loading rates and cumulative zinc load

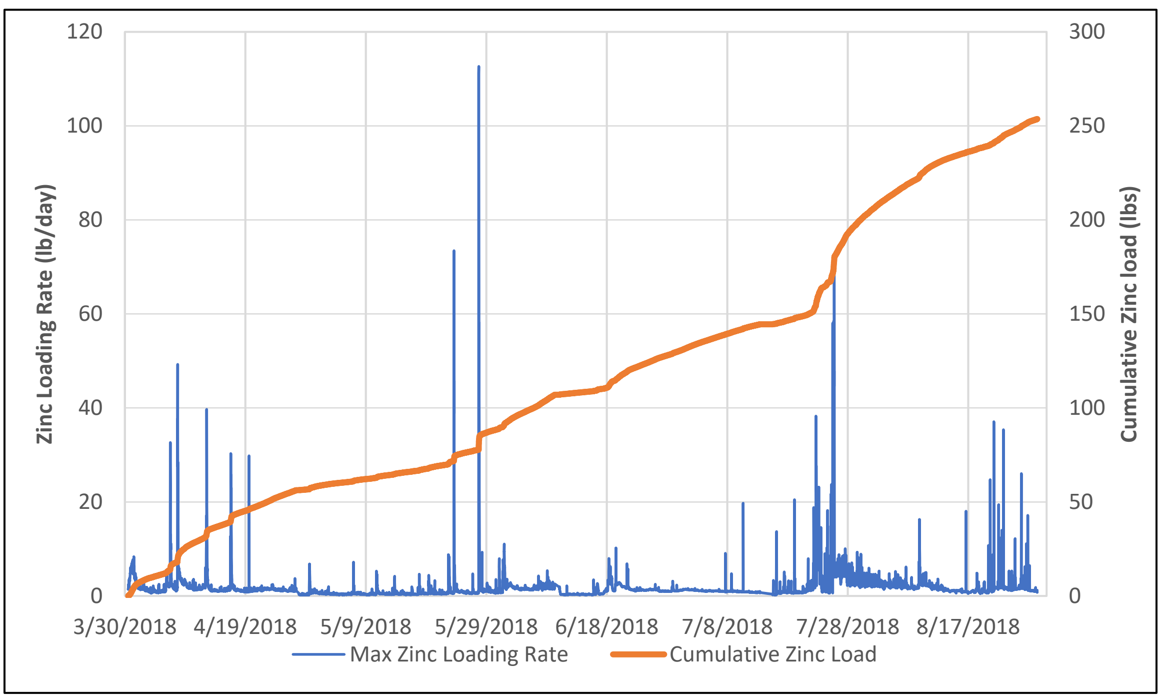


Figure 48: Calculated average zinc loading rates and cumulative zinc load

8.2. Soil and Sediment Samples QA/QC

Table XXIII: Percent Difference Between MARCOM and EENV (MARCOM as standard)

Sample	As	Cu	Fe	Pb	Zn
GGSDS-17	25%	21%	45%	34%	45%
GGSS-03	4%	22%	30%	7%	27%
GGSS-05	-5%	-1%	16%	-4%	3%
GGSS-06	31%	39%	35%	27%	33%
GGSS-07	19%	24%	34%	19%	10%
GGSS-11	42%	50%	26%	10%	6%
GGSS-13	36%	30%	32%	24%	26%
GGSS-14	34%	61%	33%	41%	52%
GGSDS-15	36%	52%	50%	53%	55%
GGSDS-18	-14%	-24%	30%	-63%	46%
GGSDS-29	16%	32%	35%	30%	49%

Samples analyzed by the Environmental Engineering Department were more conservative or underestimated when compared to MarCOM Lab's shown by the positive percentages in Table XXIII.

8.3. Water Sample Field and Lab Duplicate QA/QC

Table XXIV: Water Sample Field and Lab Duplicate Percent Difference

Site	Date	Type	Original					Duplicate				
			As	Cu	Fe	Pb	Zn	As	Cu	Fe	Pb	Zn
GG-07	11/17/2017	Field DP	11		3.381	1.6	100.8	11.5		3.252	1.4	100
GG-06	10/5/2017	Field DP	4.9				11.5	4.7				11.6
GG-05	12/11/2017	Field DP	12.3		3.534	1.06	117.3	11.8		3.699	1.1	98.4
GG-06	11/17/2017	Lab DP	2.14	0.39	0.1091	1.06	50.7	2.14	0.39	0.1107	1.06	51.3
GG-04	12/11/2017	Lab DP	9.6	10.6	5.346	36.6	234.2	9.9	10.4	5.457	36.1	239.2
SW2	4/29/2018	Lab DP	2.14	65.2	0.7079	8.1	185.6	2.14	13.1	0.2331	5.2	586.1
GG-07	9/13/2018	Lab DP	1.8	37.1	6.032	4.8	2465	16.7	38.7	5.587	4.8	2522
GG-07	6/5/2018	Lab DP	11.4	112.1	3.424	3.7	896.4	11.2	110.9	3.278	4.2	1063
GG-03	6/5/2018	Lab DP	2.14	268.6	0.494	1892	95	2.5	267	0.4783	1833	93.9

Site	Date	Type	Percent Difference for Duplicates				
			As	Cu	Fe	Pb	Zn
GG-07	11/17/2017	Field DP	-5%	--	4%	13%	1%
GG-06	10/5/2017	Field DP	4%	--	--	--	-1%
GG-05	12/11/2017	Field DP	4%	--	-5%	-4%	16%
GG-06	11/17/2017	Lab DP	0%	0%	-1%	0%	-1%
GG-04	12/11/2017	Lab DP	-3%	2%	-2%	1%	-2%
SW2	4/29/2018	Lab DP	0%	80%	67%	36%	-216%
GG-07	9/13/2018	Lab DP	-828%	-4%	7%	0%	-2%
GG-07	6/5/2018	Lab DP	2%	1%	4%	-14%	-19%
GG-03	6/5/2018	Lab DP	-17%	1%	3%	3%	1%

8.4. ICP-OES Calibration Pass-Fail QA/QC

Table XXV: ICP-OES Pass/Fail QA/QC

ICP-OES Run Date	CCV	ICV	CCB	If Fail what Element
	P/F	P/F	P/F	
3/8/2018	P	P	P	N/A
3/13/2018	P	P	P	N/A
4/12/2018	P	P	P	N/A
4/19/2018	P	P	P	N/A
4/26/2018	P	P	P	N/A
6/9/2018	P	P	P	N/A
7/14/2018	P	P	P	N/A
8/2/2018	P	P	P	N/A
9/17/2018	F	P	P	Calcium Failed
9/25/2018	F	P	P	Calcium Failed
11/2/2018	P	P	P	N/A

9. Appendix B: Raw Data and Calculations

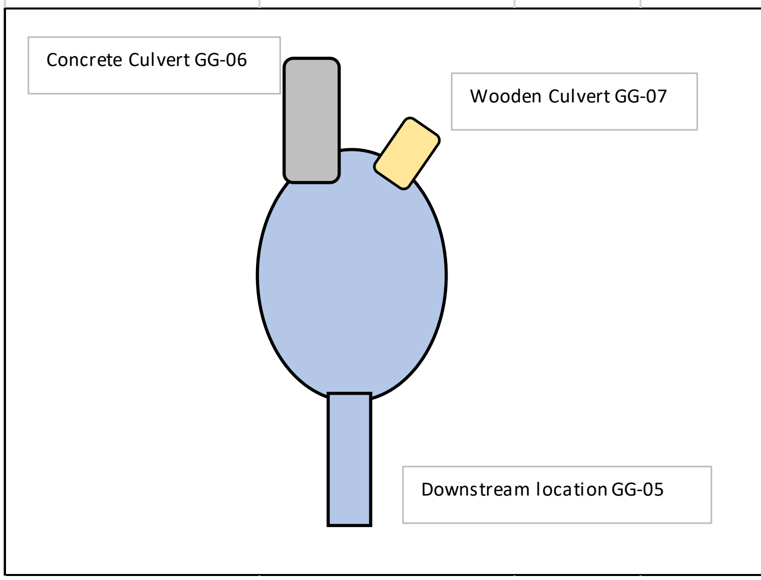
9.1. Flow Rate and Loading Rate Calculations for Culverts

Table XXVI: Water balance and loading rates for culverts and GG-05

Flow and loading rate calculations for 9/27/18						
FLOW -Q		**flow**	**unit**			
GG-06	Q1	0.33	cfs			
GG-05	Q2	0.6826	cfs		0.516554	
GG-07*	Q3	0.3526	cfs			
CONCENTRATION - C		**As**	**Cu**	**Pb**	**Zn**	**unit**
GG-06	C1	1.8	8.2	2.3	16.4	ug/L
GG-05	C2	3	51	3.1	872.6	ug/L
GG-07	C3	12.8	8.5	2.6	2506	ug/L
GG-05*	C4	7.482098	8.354966	2.454966	1302.414	ug/L
Loading Rates lb/day		**As**	**Cu**	**Pb**	**Zn**	**unit**
GG-06	T1	0.0027	0.0121	0.0034	0.0243	lb/day
GG-05	T2	0.0092	0.1563	0.0095	2.6734	lb/day
GG-07	T3	0.0203	0.0135	0.0041	3.9660	lb/day

Conversions		
From	**multiply**	**To**
cfs	0.538171391	MGD
ug/L	0.001	mg/L

Water Balance
Q3 = Q2 - Q1
GG-05 Concentration
C4 = ((C1 x Q1) + (C2 x Q3)) /Q2
Loading Rate
lb/day = (Qx0.53817)*(C/1000)*8.34



9.2. Grove Gulch & BTC Loading Rate Calculations

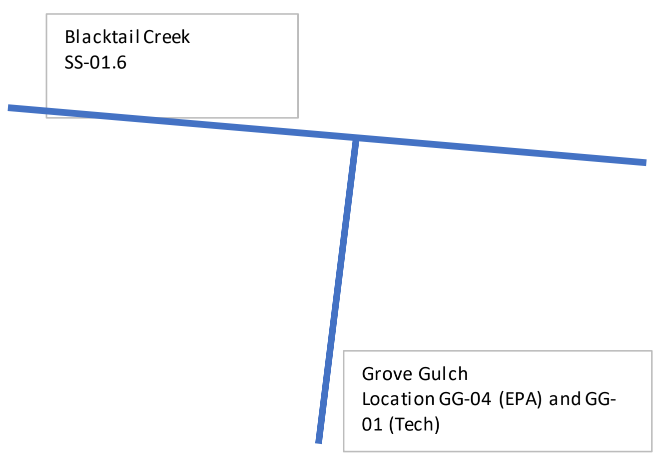
Table XXVII: Loading rate calculations for Grove Gulch and BTC

Average Loading rate calculations for GG and BTC			
FLOW -Q		**flow**	**unit**
GG-01	Q1	0.43	cfs
GG-04*	Q2	0.3	cfs
SS-01.6*	Q3	0.63	cfs
CONCENTRATION - C		**Zn**	**unit**
GG-01	C1	196.2	ug/L
GG-04*	C2	43	ug/L
SS-01.6*	C3	8.2	ug/L
Loading Rates lb/day		**Zn**	**unit**
GG-01	T1	0.3787	lb/day
GG-04*	T2	0.0579	lb/day
SS-01.6*	T3	0.0232	lb/day

* = Data provided by EPA

Conversions		
From	**multiply**	**To**
cfs	0.538171391	MGD
ug/L	0.001	mg/L

Water Balance
Q3 = Q2 - Q1
GG-05 Concentration
C4 = ((C1 x Q1) + (C2 x Q3)) /Q2
Loading Rate
lb/day = (Qx0.53817)*(C/1000)*8.34



9.3. Sulfate-Reducing Bio-Reactor Calculations

Table XXVIII: Sulfate-Reducing Bio-Reactor Size Calculations

Design Recommendations			
Assumed Sulfate Reduction Rate	300	mmol/m3/day	Notes: Flow rate was obtained from field data in september 27th 2018. Water quality data was abtained from water sampling.

Inputs		
Flow	0.35	cfs
Flow	856,301.44	L/day
pH	6.75	
Cu	0.04	mg/L
Zn	1.88	mg/L
Fe	5.37	mg/L

Divalent Metals Table					
	MW	mmol/L	Sulfate Reduction Required in molar basis		
Cu	63.546	0.000705001	1	0.00071	mmol/L
Zn	65.409	0.028719289	1	0.02872	mmol/L
Fe	55.845	0.096201988	1.5	0.14430	mmol/L
pH			0.5	0.00009	mmol/L
				0.17382	mmol/L

Required Sulfate		
Reduction Rate	148839.1	mmol/day
Volume of Substrate	496.1	m3
	496130.2	L
Residence Time	0.579387	days
Wood Chip Hydraulic Conductivity	0.25	cm/sec
	216	m/day
Length	20	m
Width	15	m
Depth	2	m
Volume	600	m3
new residence time	0.70	days

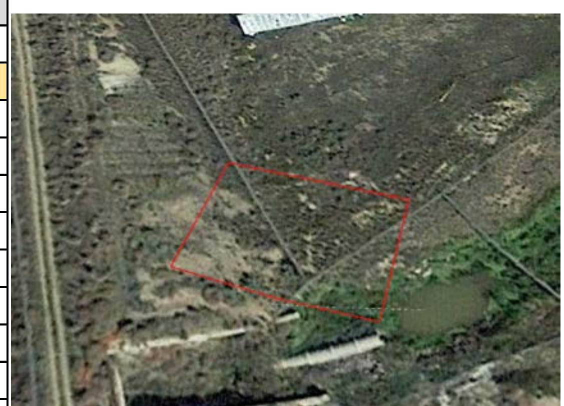


Table XXIX: Sulfate-Reducing Bio-Reactor Size Calculations

Sulfate-Reducing Bio-Reactor Cost Estimate						
Item	Volume Needed		Cost	unit	Total Cost	Comments
Wood Chips	780	yrd3	$ 15.00	$/yrd3	$ 11,700.00	
Lime stone	324	tons	$ 27.50	$/ton	$ 8,910.00	Bottom depth (0.3636 m) , top depth (0.061 m) 2700 lb/yrd3
Gravel bed	120	yrd3	$ 30.00	$/yrd3	$ 3,600.00	0.3048m x 20m x 15m
30 mil liner	6245	ft2	$ 0.50	$/ft2	$ 3,122.50	https://www.homeadvisor.com/cost/landscape/pond-liner-prices/
Drain Pipe	21	sections	$ 10.00	$/section	$ 210.00	
4" elbow pvc	2	units	$6	$/unit	$ 12.00	10' by 4" PVC drain pipe
4" to 8" pvc reducer	3	units	$ 10.00	$/unit	$ 30.00	
8" PVC DWV 45 degree elbow	2	units	$ 65.00	$/unit	$ 130.00	
8 in. PVC DWV Wye	2	units	$ 123.00	$/unit	$ 246.00	
8' PVC Pipe 10'	3	sections	$ 90.00	$/section	$ 270.00	https://pvcpipesupplies.com/8-x-10-schedule-40-pvc-pipe-h0400800pw1000.html
				Total:	$ 28,230.50	

Reactor bed depths								
Limestone	0.5	ft	45.72	m3	59.79	yrd3		
Woodchips	6.5	ft	594.36	m3	777.39	yrd3		
Limestone	1.5	ft	137.16	m3	179.40	yrd3	324	tons
Gravel	1	ft	91.44	m3	119.60	yrd3		

Liner surface area calc		
30 mil liner m2		
base	300	
sides	140	
lip	70	
anchor	70	
	580	m2
	6243.068042	ft2

SIGNATURE PAGE

This is to certify that the thesis prepared by Westley Lund entitled "Remediation Investigation and Feasibility Study for "In-Place" Mine Waste Influenced Grove Gulch, Butte, MT" has been examined and approved for acceptance by the Department of Environmental Engineering, Montana Technological University, on this 4th day of December, 2018.

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